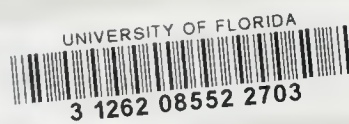


CORRESPONDING STATES RELATIONSHIPS  
FOR TRANSPORT PROPERTIES OF  
PURE DENSE FLUIDS

By  
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## PREFACE

An important consideration for the chemical engineer is his ability to predict reliable values for various properties of chemical substances that are needed for design equations. Because of the large number of combinations of substances, compositions, pressures, temperature, etc., that may be encountered, it is often neither feasible nor desirable to make experimental measurements of such properties. The need for reliable correlations has become more acute with the increasing use of high-speed electronic computers in designing chemical plants. Such design requires suitable mathematical expressions for properties as a function of operating conditions. Even when experimental data in tabulated form are available it is most conveniently introduced into the computer in the form of soundly based theoretical equations.

In the long term the only satisfactory approach is one that is firmly based on molecular considerations. Theories for dilute fluids are well established. The kinetic theory of gases is capable of describing the thermodynamic and transport properties accurately. However, for dense fluids there is still no theory which can parallel the success of the dilute gas theory. Although there are several rigorous molecular theories for liquids, none have yet been developed to a stage that would yield numerical results.

Theoretical study of transport properties is more difficult than that of thermodynamic properties. In thermodynamics, all equilibrium properties can be obtained once the partition function

of the system is known. However, for transport processes each of the transport properties has to be formulated separately. This situation occurs because the thermodynamic equilibrium state is unique, whereas there are many types of non-equilibrium state.

This dissertation considers corresponding states correlations of transport properties of fluids, particularly liquids. This principle has previously proved of great value to engineers in predicting thermodynamic properties. Chapter 1 provides a brief survey of the present status of theories of transport properties of dense fluids. Chapters 2-4 contain a detailed study of the free volume theory of viscosity and self-diffusion coefficient, with particular emphasis on developing corresponding states relations for the parameters involved. The next two chapters discuss a more direct corresponding states treatment, and a new theory is proposed for polyatomic molecules.

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# LIST OF SYMBOLS

$A$	= pre-exponential factor of free volume equation for viscosity
$A_0$	= $A/T^{1/2}$
$A_1, A_2, A_3, A_4$	= arbitrary constants
$A'_1, A'_2$	= constants
$A', A''$	= constants
$a_1, a_2, a_3, a_4, a_5$	= coefficients of viscosity equation
$a^*$	= molecular diameter
$B$	= pre-exponential factor of free volume equation for self-diffusivity
$B_0$	= $B/T^{1/2}$
$B_0^*$	= $(B_0 m^{1/2})/(\sigma k^{1/2})$
$B_1, B_2, B_3, B_4$	= arbitrary constants
$B', B''$	= constants
$B_a$	= arbitrary constant
$b_0$	= the rigid sphere second virial coefficient
$b_1, b_2, b_3, b_4, b_5$	= coefficients of thermal conductivity equation
$C_1$	= empirical constant
$C_a$	= arbitrary constant
$c$	= a characteristic factor defined by equation (6.37)
$c_0$	= total concentration
$c_1$	= $v/r_1^3$ = constant
$c_2$	= $(r_2/r_1)^3$ = constant
$c_3$	= $(c_1 \sigma^3/v_m)$ = constant
$c_4$	= $\epsilon/kT_m$ = constant

$D$	= self-diffusion coefficient
$D_{AB}$	= binary diffusion coefficient
$D^*$	= $D_m^{1/2}/\sigma\epsilon^{1/2}$ = reduced self-diffusivity by simple correspondence principle
$\tilde{D}^*$	= $D_m^{1/2}/c\sigma\epsilon^{1/2}$ = reduced self-diffusivity by proposed correspondence principle
$D_{AB}^*$	= reduced mutual diffusion coefficient defined by equation (5.33)
$d$	= distance of closest approach of 2 molecules
$d_1, d_2$	= coefficients of self-diffusivity equation
$\langle E_i \rangle$	= average total energy of molecule $i$
$E_v$	= activation energy at constant volume
$E_v^*$	= $E_v/RT_m$ = reduced activation energy
$e$	= varying activation energy per molecule
$\langle e \rangle$	= average activation energy per molecule
$e_j$	= energy level
$e_o$	= height of potential barrier in equilibrium liquid
$e_v$	= $E_v/\tilde{N}$
$F_{iy}$	= y-component of intermolecular force on molecule $i$
$\bar{f}^{(1)}$	= time smoothed singlet distribution function
$\bar{f}^{(2)}$	= time smoothed pair distribution function
$f_1$	= a function of density given by equation (1.23)
$g$	= universal function
$g_o(r)$	= equilibrium radial distribution function
$g_1$	= geometric factor
$H$	= Hamiltonian

$H_{CM}$	= Hamiltonian of center of mass coordinates
$h$	= Planck constant
$h^*$	= $h/(\sigma\sqrt{m\epsilon})$ = reduced Planck constant
$I$	= moment of inertia
$I_1$	= viscosity constant used in equation (1.22)
$J^{xx}$	= defined by equation (1.6)
$J^{xy}$	= defined by equation (1.5)
$K$	= kinetic energy
$K_{CM}$	= kinetic energy of center of mass coordinates
$K_{rot}$	= kinetic energy of rotational motion
$K_1$	= $(n/n-6)(n/6)^{6/(n-6)}$
$k$	= Boltzmann constant
$k_{11}$	= defined by equation (6.8)
$k_{12}$	= defined by equation (6.9)
$k_{22}$	= defined by equation (6.10)
$L$	= Lagrangian
$l$	= jump distance
$M$	= molecular weight
$M_A$	= molecular weight of component A
$M_B$	= molecular weight of component B
$m$	= mass of molecule
$N$	= number of molecules
$\sim N$	= Avogadro number
$n$	= repulsive exponent in $[6,n]$ potential law
$n_1$	= singlet number density

$P$	= pressure
$P_c$	= critical pressure
$P_{cAB}$	= critical pressure of a mixture A-B
$P^*$	= $P\sigma^3/\epsilon$ = reduced pressure by simple correspondence principle
$\tilde{P}^*$	= $P\sigma^3/c\epsilon$ = reduced pressure by improved correspondence principle
$p$	= momentum
$p_{ix}$	= momentum in x-direction of molecule i
$p_p^{(i)}$	= probability of a molecule having activation energy $e_i$ and free volume $v_p$
$p^*$	= $p/(m\epsilon)^{1/2}$ = reduced momentum
$Q$	= partition function
$Q^*$	= defined by equation (5.35)
$q_f$	= thermodynamic free volume
$\underline{r}$	= position vector
$\underline{r}_{ij}$	= $\underline{r}_j - \underline{r}_i$
$r^*$	= $r/\sigma$ = reduced distance
$(s/c)_k$	= a constant factor used by Hermesen and Prausnitz (166)
$s^*$	= defined by equation (1.7)
$T$	= temperature
$T_c$	= critical temperature
$T_{cAB}$	= critical temperature of a mixture A-B
$T_m$	= melting temperature
$T^*$	= $kT/\epsilon$ = reduced temperature by simple correspondence principle



$\tilde{T}^*$	= $kT/c\epsilon$ = reduced temperature by improved correspondence principle
$\tilde{T}$	= $kT/[\epsilon(s/c)_k]$ = reduced temperature used by Hermesen and Prausnitz (166)
$t$	= time
$t^*$	= $t\epsilon^{1/2}/\sigma_m^{1/2}$ = dimensionless time
$U(r)$	= $\sum_{i < j}^N u(r_{ij})$ = pair potential
$U(0,0)$	= potential energy of a molecule at the center of a cell
$U(x, \Psi_x)$	= potential energy of a molecule in a cell
$U(x_1, \dots, x_N)$	= potential energy of N molecules
$U(0)$	= potential energy of N molecules at the centers of their cells
$V$	= molal volume
$\underline{V}$	= velocity vector
$V_f$	= molal free volume
$V_x$	= velocity in the x-direction
$V^*$	= $(V/\sigma^3)$ = reduced molal volume
$V_k^*$	= characteristic volume used by Hermesen and Prausnitz (166)
$\tilde{V}^*$	= $V/V_m$
$\tilde{V}_k$	= $V/V_k^*$ = reduced volume of Hermesen and Prausnitz (166)
$V_o$	= minimum free volume per mole needed for molecular flow to occur
$V_o^*$	= $V_o/\sigma^3$ = reduced minimum free volume
$V_o^1$	= minimum free volume when $T^* = 1.0$
$V_o^{1*}$	= $V_o^1/V_m$ = reduced minimum free volume when $T^* = 1.0$

$v$	$= V/\tilde{N}$ = average volume per molecule
$v_f$	$= v - v_o$ = free volume
$v_m$	$= V_m/\tilde{N}$
$v^*$	$= V^*/\tilde{N}$
$\tilde{v}$	= varying free volume
$v_\sigma^*$	$= (d/\sigma)^3$
$v_o$	$= V_o/\tilde{N}$ = minimum free volume per molecule needed for molecule flow to occur
$W_1, W_2$	= number of configurations for distribution of molecules
$x_i$	= x-component of position vector $\underline{r}_i$ of molecule i
$Y$	= average percent error (see page 80)
$y$	$= b_o \chi/V$
$Z$	= configurational partition function
$z$	= number of nearest neighbors in a ring
$\alpha$	= Lagrange multiplier
$\beta$	$= 1/kT$ = Lagrange multiplier
$\gamma$	= free volume overlap factor
$\epsilon$	= characteristic energy parameter in [6,n] potential
$\zeta$	= molecular friction constant
$\eta$	= shear viscosity
$\eta_o$	= dilute gas viscosity
$\eta^*$	$= \eta \sigma^2 / (m\epsilon)^{1/2}$ = reduced shear viscosity by simple correspondence principle
$\tilde{\eta}^*$	$= \eta \sigma^2 / c(m\epsilon)^{1/2}$ = reduced shear viscosity by improved correspondence principle
$\eta_o^*$	= defined by equation (5.36)
$\underline{\theta}$	= angle vector (in terms of Eulerian angles $\theta, \phi, \psi$ )

$\theta_x$	= x-component of an angular rotation
$\kappa$	= bulk viscosity
$\kappa^*$	= $\kappa \sigma^2 / (m\epsilon)^{1/2}$ = reduced bulk viscosity by simple correspondence principle
$\tilde{\kappa}^*$	= $\kappa \sigma^2 / c(m\epsilon)^{1/2}$ = reduced bulk viscosity by improved correspondence principle
$\Lambda$	= Lagrange multiplier
$\lambda$	= thermal conductivity
$\lambda_o$	= dilute gas thermal conductivity
$\lambda^*$	= $\lambda \sigma^2 m^{1/2} / k\epsilon^{1/2}$ = reduced thermal conductivity by simple correspondence principle
$\tilde{\lambda}^*$	= $\lambda \sigma^2 m^{1/2} / ck\epsilon^{1/2}$ = reduced thermal conductivity by improved correspondence principle
$\Xi$	= $B'/A'$ = constant
$\xi$	= constant
$\pi$	= a constant which has a value of 22/7
$\rho$	= density
$(\rho D)_o$	= value of the product of density and self-diffusivity of a dilute gas
$\rho^*$	= reduced density
$\sigma$	= characteristic distance parameter in [6,n] potential
$\sigma_1, \sigma_2$	= characteristic distance parameter in square-well potential
$\Phi$	= a universal potential energy function
$\dot{\Phi}_x$	= angle associated with constant angular velocity
$\phi$	= a universal function
$\chi$	= a factor defined by equation (1.13)
$\chi_h$	= probability of hole formation

$\Psi_x$	=	angle associated with superimposed angular velocity
$\psi_0, \psi_2$	=	the radial functions in the spherical harmonic expansion of the nonequilibrium distribution function $g(r)$
$\Omega^{(1,1)*}, \Omega^{(2,2)*}$	=	dimensionless collision integrals
$\omega$	=	Pitzer factor
$\underline{\omega}$	=	angular velocity
$\omega_1$	=	angular velocity in a harmonic motion

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CORRESPONDING STATES RELATIONSHIPS FOR TRANSPORT  
PROPERTIES OF PURE DENSE FLUIDS

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Two approaches have been considered for developing corresponding states correlations for dense fluid transport properties. The first is based on the free volume theory for viscosity and self-diffusion coefficient. This theory has been improved to account quantitatively for the nonlinearity of constant volume plots of  $\ln(\eta/T^{1/2})$  vs.  $T^{-1}$  and  $\ln(D/T^{1/2})$  vs.  $T^{-1}$  for simple liquids, by the introduction of the temperature dependence of  $V_0$  and the volume dependence of  $E_v$ . Corresponding states relations are presented for these two quantities. The improved free volume theory accurately describes the viscosity and self-diffusion coefficient behavior of liquids composed of simple, nonpolar molecules that may be expected to approximately obey a Lennard-Jones [6,12] potential law, for the density range of  $\rho > 2\rho_c$ . It is in this range that most other theories fail. The only parameters required for the viscosity and self-diffusion coefficient prediction are melting and critical parameters, together with one experimental value of viscosity (or self-diffusivity).

Direct corresponding states correlations of transport properties have also been studied, and provide a more general if slightly less accurate method of prediction. The simple corresponding states principle derived by Helfand and Rice from the time correlation function expressions of statistical mechanics has been shown to apply closely for the transport properties of monatomic molecules over the entire range of temperature and density conditions for which measurements are available. In this simple form, however, it was found not to apply to polyatomic fluids in the dense phase. After careful re-examination of the four assumptions on which the derivation of the simple correspondence principle is based, it is shown that hindered rotation at high density is the most probable cause for the deviation of polyatomic fluids from the correspondence principle.

A correspondence principle for polyatomic molecules has been derived, taking into account the effects of hindered rotation and making use of a simple harmonic oscillator model. The proposed equations have been tested exhaustively for the viscosity, thermal conductivity and self-diffusion coefficient of a large number of polyatomic fluids over a wide range of temperature and density conditions. The molecules tested include saturated hydrocarbons from methane to nonane, spherical molecules such as neopentane and carbon tetrachloride, flat molecules such as benzene, and simple diatomic molecules such as nitrogen. The improved correspondence principle predicts the transport properties of saturated liquids within experimental error. For high pressures the average percentage errors of the predicted viscosity and thermal conductivity are slightly higher.

It is also shown that the proposed model can account in a reasonable way for thermodynamic properties of polyatomic fluids.

## CHAPTER 1

### INTRODUCTION

In this chapter a brief survey and evaluation is presented of the principal theories and empirical correlations that have been proposed to explain dense fluid transport properties. For pure fluids all transport properties are functions of temperature and density, namely,  $\eta = \eta(T, \rho)$ ,  $\kappa = \kappa(T, \rho)$ ,  $D = D(T, \rho)$  and  $\lambda = \lambda(T, \rho)$ . None of the present theories provide a satisfactory means of predicting transport properties over the entire range of temperature and density conditions for even quite simple fluids. Also assumptions of dubious validity must be made in most cases in order to be able to make any comparison with experiment at all. In the following survey the more rigorous approaches are first described, followed by simple model theories and ending with the empirical correlations.

#### 1.1 The Time Correlation Function Theory

In the last decade a new theory, called the time correlation function theory (also known as the fluctuation-dissipation theory) has been developed to treat transport processes. This theory treats transport processes in terms of equilibrium ensembles whose properties are known. In a sense the time correlation function plays a similar role to the partition function in statistical thermodynamics. In statistical thermodynamics, all thermodynamic properties of any particular system can be evaluated if the partition function is known. In the same manner the transport coefficients can be obtained if the appropriate time correlation functions can be calculated. However, in



one respect the analogy breaks down. In statistical thermodynamics a single partition function determines all the thermodynamic properties, whereas in transport processes different time correlation functions are needed for different transport processes. A good review of the time correlation function approach to transport processes is given by Zwanzig (1).

The time correlation function expressions for the transport coefficients may be derived by several methods. A simple derivation involves starting with expressions analogous to the Einstein equation for the self-diffusion of Brownian particle (2). The following expressions for transport coefficients are obtained.

$$\text{Self-diffusion coefficient} \quad D = \int_0^{\infty} \langle V_x(0) V_x(t) \rangle dt \quad (1.1)$$

$$\text{Shear viscosity} \quad \eta = \frac{1}{V k T} \int_0^{\infty} \langle J^{xy}(0) J^{xy}(t) \rangle dt \quad (1.2)$$

$$\text{Bulk viscosity} \quad \kappa = \frac{1}{V k T} \int_0^{\infty} \langle J^{xx}(0) J^{xx}(t) \rangle dt \quad (1.3)$$

$$\text{Thermal conductivity} \quad \lambda = \frac{1}{V k T^2} \int_0^{\infty} \langle S^x(0) S^x(t) \rangle dt \quad (1.4)$$

where  $V_x(t)$  = velocity in the x-direction at time  $t$

$$J^{xy} = \sum_{i=1}^N \left[ \frac{p_{ix} p_{iy}}{m} + x_i F_{iy} \right] \quad (1.5)$$

$$J^{xx} = \sum_{i=1}^N \left[ \frac{p_{ix} p_{ix}}{m} + x_i F_{ix} \right] - PV \quad (1.6)$$

$$S^x = \sum_{i=1}^N \left[ \frac{p_{ix} p_{ix}}{2m} - \langle E_i \rangle_{xx} \right] + \frac{1}{2} \sum_{j=1}^N \left[ u(r_{ij})_{xx} + x_{ij} F_{ijx} \right] + \frac{p_{ix}}{m} - \frac{PV}{Nm} \sum_{i=1}^N p_{ix} \quad (1.7)$$

For dilute gases the time correlation functions may be evaluated and the expressions for the transport coefficients can be reduced to the forms obtained by solving the Boltzmann equation. However, for dense fluids no satisfactory expressions have as yet been obtained, although several approximate equations have been suggested (3). One approach has been to assume that the time correlation function decays exponentially. Alternatively one may perform molecular dynamics calculations (4-6). In this method a very large amount of computation is involved; the principal interest of such an approach is to provide data with which to compare various theoretical expressions for the time correlation functions.

The time correlation theory gives a formal description of transport processes; however it is still not developed to a sufficiently advanced stage to be of practical value in the calculation of transport coefficients. To the chemical engineer, the most interesting feature of the theory in its present state of development is that it provides the basis for a rigorous development of the corresponding states principle for dense fluid transport properties. This is discussed in a later section of this chapter.

## 1.2 The Kinetic Theory of Liquids

The kinetic theory of dilute gases is already very well developed (7), and provides a method of accurately estimating their transport properties. It is therefore reasonable to attempt a similar development for dense gases and liquids. Such an attempt was first made by Kirkwood (8,9), whose approach was based on casting the

Liouville equation for the distribution function into an equation of the Fokker-Planck type. The main disadvantage in this theory is that a large number of approximations have to be made in obtaining the Fokker-Planck equations for  $\bar{f}^{(1)}$  and  $\bar{f}^{(2)}$ , the time smoothed singlet and pair distribution functions respectively. In addition to these deficiencies, Kirkwood's method has drawn much criticism for assuming the mean momentum change for a collision to be small. The equations derived by the method of Irving and Kirkwood (9) for transport coefficients of liquids are as follows (10)

Shear viscosity

$$\eta = \frac{n_1 m k T}{2\zeta} + \frac{\pi \zeta}{15 k T^2} \int_0^\infty r^3 \frac{du(r)}{dr} g_o(r) \psi_2(r) dr \quad (1.8)$$

Bulk viscosity

$$\kappa = \frac{\pi \zeta n_1^2}{9 k T} \int_0^\infty r^3 \frac{du(r)}{dr} g_o(r) \psi_o(r) dr \quad (1.9)$$

Thermal conductivity

$$\lambda = \frac{5 k^2 n_1 T}{6 \zeta} + \frac{n_1^2 \pi k T}{\zeta} \left[ \frac{1}{3} \int_0^\infty \left( r \frac{\partial u(r)}{\partial r} - u(r) \right) g_o(r) \frac{d}{dr} \left( \frac{\partial \log g_o(r)}{\partial T} \right) r^3 dr + \int_0^\infty \left[ u(r) - \frac{1}{3} r \frac{\partial u(r)}{\partial r} \right] \frac{\partial g_o(r)}{\partial T} r^2 dr \right] \quad (1.10)$$

Self-diffusion coefficient  $D = \frac{k T}{\zeta}$  (1.11)

where

$$\zeta^2 = \frac{4\pi}{3} \rho \int_0^\infty r^2 g(r) \nabla^2 u(r) dr \quad (1.12)$$

and  $\psi_o, \psi_2$  = the radial functions in the spherical harmonic expansion of the nonequilibrium distribution function  $g(r)$

A modification of the Kirkwood theory due to Rice and Allnatt (11,12) attempts to avoid the assumption that the mean collisional

momentum change is small. In the Rice-Allnatt theory, a potential energy function is assumed in which the molecule has a hard core together with an outer shell which interacts with a soft attractive potential. A hard core collision leads to a large momentum transfer and tends to vitiate the Brownian motion approximation which is inherited in the Fokker-Planck equation. These authors therefore treated the rate of change of the distribution function  $\bar{f}$  due to hard core collisions by means of an Enskog-type collision term, and treated the rate of change of the distribution function due to motion in the attractive field of surrounding molecules between collision by Kirkwood's approach.

In order to calculate the transport coefficients from the Kirkwood or Rice-Allnatt theory one must have accurate values for the intermolecular potential, and also the equilibrium radial distribution function has to be known quantitatively. The latter requirement is especially difficult to meet since the experimental radial distribution function has not been determined accurately.

Making use of the Kirkwood theory, Zwanzig, Kirkwood, Stripp and Oppenheim (13) were able to calculate the shear viscosity and bulk viscosity for liquid argon near the boiling point. Their calculated value for shear viscosity was  $\eta = 0.73 \times 10^{-3}$  poise, while the experimental value of shear viscosity for argon at the same temperature is  $\eta = 2.39 \times 10^{-3}$  poise. Thus the calculated value is in error by roughly a factor of three. For bulk viscosity, their computation yielded  $\kappa = 0.36 \times 10^{-3}$  poise. However, according to Naugle's (14) measurement of bulk viscosity for liquid argon at approximately the same temperature,

$\kappa = 1.7 \times 10^{-3}$  poise. The discrepancy between calculated and experimental values is more than a factor of four. Because of the non-trivial mathematics involved, the Kirkwood theory has not been tested for the temperature and density dependence even for very simple molecules such as argon.

The Rice-Allnatt theory has been tested by Lowry, Rice and Gray (15) for viscosity. They found quite good agreement between calculated and experimental values of argon at densities slightly less than the normal liquid density (Table 1.1). To compare theory and experiment they assumed  $u(r)$  to be given by the Lennard-Jones [6,12] potential. The radial distribution functions,  $g(r)$  for different temperatures were those obtained theoretically by Kirkwood, Lewinson and Alder (16). The radial distribution functions  $g(r)$  and the derivative of  $u(r)$  were modified by introducing an empirical parameter  $c_1$ , which was obtained from equation of state data.

TABLE 1.1

TEST OF RICE-ALLNATT THEORY FOR  
SHEAR VISCOSITY OF ARGON

	$\eta \times 10^3$ , poise			
Density, $\text{gcm}^{-3}$	1.12			1.375
Temperature, $^{\circ}\text{K}$	128	133.5	185.5	90
Pressure, atm.	50	100	500	1.3
$c_1$	0.9819	0.9827	0.9887	0.9705
$\eta(\text{calc})$	0.727	0.730	0.771	1.74
$\eta(\text{expt})$	0.835	0.843	0.869	2.39
% error	13.0	13.4	11.3	27.2

Ikenberry and Rice (17) tested the Rice-Allnatt theory on the thermal conductivity of argon for the same temperature and density conditions as the viscosity values shown in Table 1.1. The calculated values were not entirely theoretical since they made use of experimental friction constants calculated from the self-diffusion coefficient data of Naghizadeh and Rice (18). Close agreement was found between theory and experiment for the entire temperature and density range considered as shown in Table 1.2.

TABLE 1.2

TEST OF RICE-ALLNATT THEORY FOR  
THERMAL CONDUCTIVITY OF ARGON

$$\lambda \times 10^4, \text{ cal.cm}^{-1}\text{sec}^{-1}\text{°C}^{-1}$$

Density, $\text{gcm}^{-3}$	<u>1.12</u>			<u>1.375</u>
Temperature, $^{\circ}\text{K}$	128	133.5	185.5	90
Pressure, atm.	<u>50</u>	<u>100</u>	<u>500</u>	<u>1.3</u>
$\lambda(\text{calc})$	2.83	1.85	1.77	1.84
$\lambda(\text{expt})$	2.96	1.89	1.86	1.87
% error	4.4	2.1	4.8	1.6

Davis, Rice and Sengers (19) further modified the Rice-Allnatt theory by using the square-well potential energy function. Because of the simple form of this function the Rice-Allnatt theory is greatly simplified and the evaluation of the pair correlation function reduces to the determination of  $g(\sigma_1)$  and  $g(\sigma_2)$ . In order to calculate the transport coefficients from this theory, one must know the values of the parameters  $\sigma_1$ ,  $\sigma_2$ ,  $\epsilon$ ,  $g(\sigma_1)$ ,  $g(\sigma_2)$  and have equation of state data.



In general  $\sigma_1$ ,  $\sigma_2$  and  $\epsilon$  for the square-well potential are available (20). In principle  $g(\sigma_1)$  and  $g(\sigma_2)$  can be calculated from equilibrium statistical mechanics. However there is still no satisfactory method of making such theoretical calculations accurately.

Davis and Luks (21) estimated the values of  $g(\sigma_1)$  and  $g(\sigma_2)$  from equation of state and thermal conductivity data of argon by solving simultaneously the modified Rice-Allnatt expressions. They then calculated the viscosity coefficient and self-diffusion coefficient of argon at various temperatures and pressures. The results are shown in Figures 1.1 and 1.2. The discrepancy between theory and experiment for viscosity is as much as 19% and for the self-diffusion coefficient is up to 34%. The experimental self-diffusivity data used by Davis et al. as shown in Figure 1.2 are apparently extrapolated values obtained from the self-diffusion coefficient data of Naghizadeh and Rice (18). Luks, Miller and Davis (22) have also made use of the modified Rice-Allnatt theory to calculate transport coefficients for argon, krypton and xenon. Discrepancies between theory and experiment become larger as the density increases.

### 1.3 The Enskog Theory (7)

Enskog extended the dilute gas kinetic theory to dense fluids composed of hard spheres. As a gas is compressed the mean free path, which for dilute gases is infinitely large with respect to the molecular diameter, gradually decreases until at high density it is of the same order of magnitude as the diameter of a molecule. During this process the intermolecular collision frequency tends to get larger due to the decrease in the mean free path; at the same time it decreases because

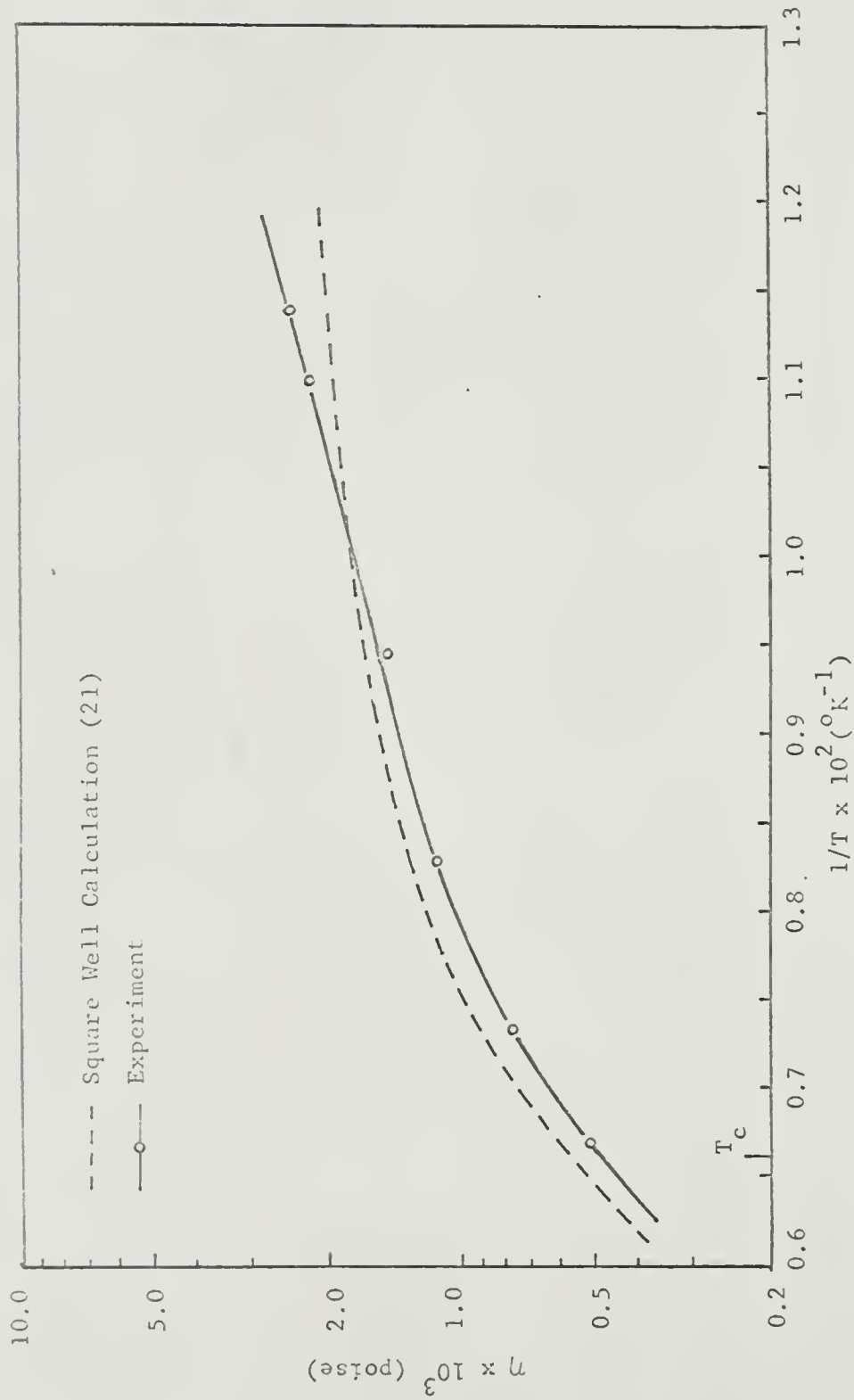


Figure 1.1. Theoretical and Experimental Saturated Liquid Viscosity of Argon - Square-Well Model.



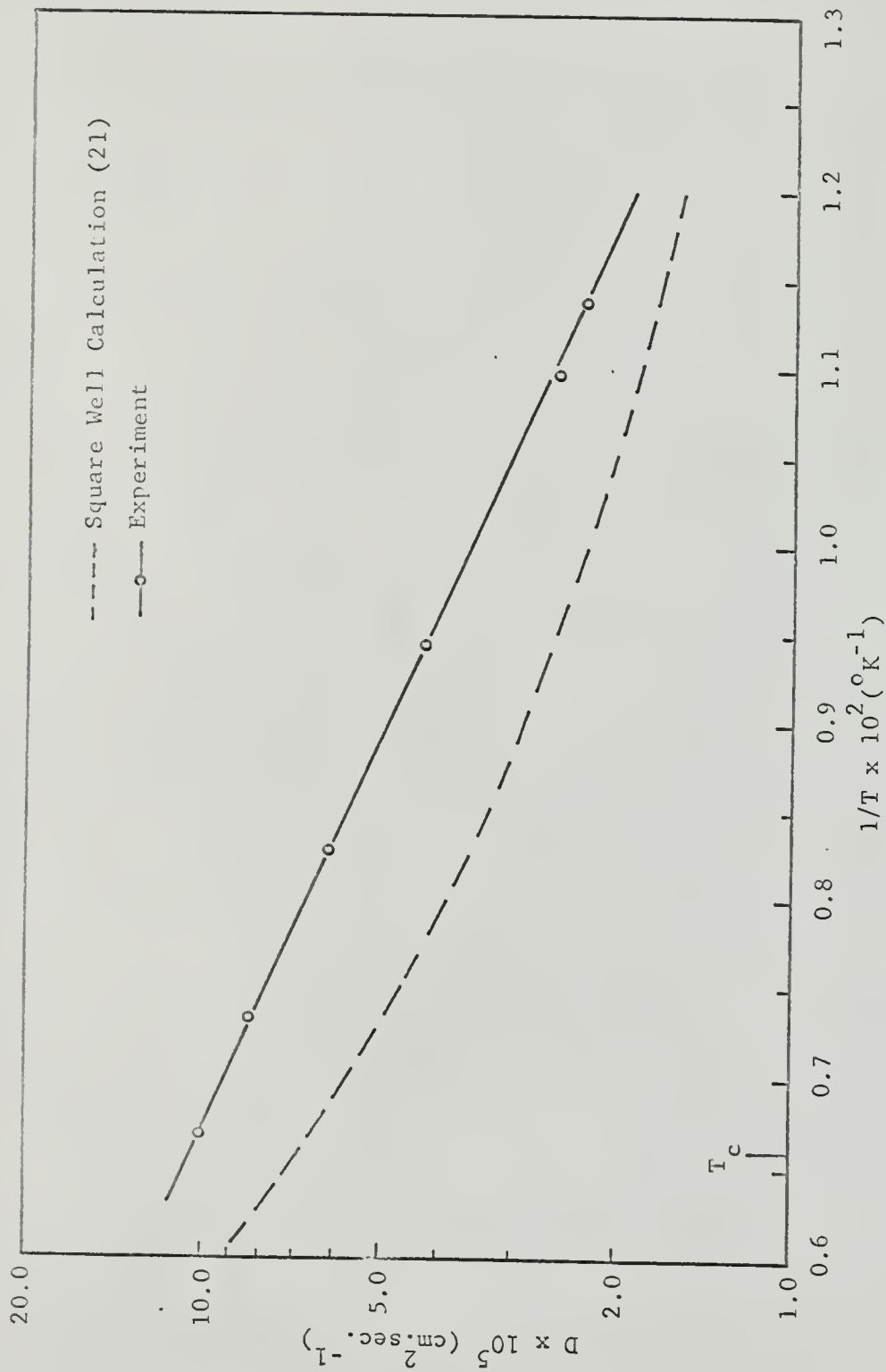


Figure 1.2. Theoretical and Experimental Saturated Liquid Self-Diffusion Coefficient of Argon - Square-Well Model.

at close separations the molecules tend to shield one another from collisions with more distant neighbors. The net change in collision frequency was found to differ from that of a dilute gas by a factor  $\chi$ , which is given by

$$\chi = 1.0 + 0.625 \left( \frac{b_o}{V} \right) + 0.2869 \left( \frac{b_o}{V} \right)^2 + 0.115 \left( \frac{b_o}{V} \right)^3 + \dots \quad (1.13)$$

where  $b_o = \frac{2}{3} \pi N \sigma^3$  = the rigid sphere second virial coefficient.

Assuming the collisional transfer of momentum and energy between colliding molecules to be instantaneous, Enskog modified the Boltzmann equation for higher densities and solved it to obtain the following equations for transport coefficients.

$$\text{Self-diffusion coefficient} \quad \frac{\rho D}{(\rho D)_o} = \frac{b_o}{V y} \quad (1.14)$$

$$\text{Shear viscosity} \quad \frac{\eta}{\eta_o} = \frac{b_o}{V} \left[ \frac{1}{y} + 0.8 + 0.761 y \right] \quad (1.15)$$

$$\text{Bulk viscosity} \quad \frac{\kappa}{\eta_o} = 1.002 \frac{b_o}{V} y \quad (1.16)$$

$$\text{Thermal conductivity (monatomic molecules)} \quad \frac{\lambda}{\lambda_o} = \frac{b_o}{V} \left[ \frac{1}{y} + 1.2 + 0.757 y \right] \quad (1.17)$$

where

$$y = \frac{b_o}{V} \chi$$

The value of  $y$  may be obtained from the equation of state by

$$\frac{PV}{RT} = 1 + y \quad (1.18)$$

Enskog suggested as an empirical modification of the hard sphere

theory the use of thermal pressure in place of external pressure.

Thus according to this modification  $y$  becomes

$$y = \frac{V}{R} \left( \frac{\partial P}{\partial T} \right)_V - 1 \quad (1.19)$$

Equations (1.15) and (1.17) predict that when  $(\eta V)$  and  $(\lambda V)$  are plotted as functions of  $y$ , the curves will go through minima at  $y = 1.146$  and  $y = 1.151$  respectively, having

$$[\eta V]_{\min} = 2.545 \eta_0 b_0 \quad \text{at } y = 1.146 \quad (1.20)$$

$$\text{and} \quad [\lambda V]_{\min} = 2.938 \lambda_0 b_0 \quad \text{at } y = 1.151 \quad (1.21)$$

In the above transport coefficient expressions,  $b_0$  is the only unknown parameter. It may be obtained from equations (1.20) and (1.21) by using experimental values of  $[\eta V]_{\min}$  and  $[\lambda V]_{\min}$ .

The Enskog dense gas theory gives a useful approximate description of transport coefficients above the critical temperature and at densities less than the critical value. The theory fails at temperatures below the critical temperature and at densities higher than the critical density. Under these conditions the rigid sphere approximation is in serious error.

The Enskog theory has been tested for thermal conductivity and viscosity of argon at various temperatures and densities (23).

Figure 1.3 shows the comparison of calculated and experimental viscosities of argon at 0°C and 75°C. The value of  $b_0$  used in these calculations was obtained from equation (1.20) using data at 0°C. The agreement between theory and experiment is moderately good at 0°C for

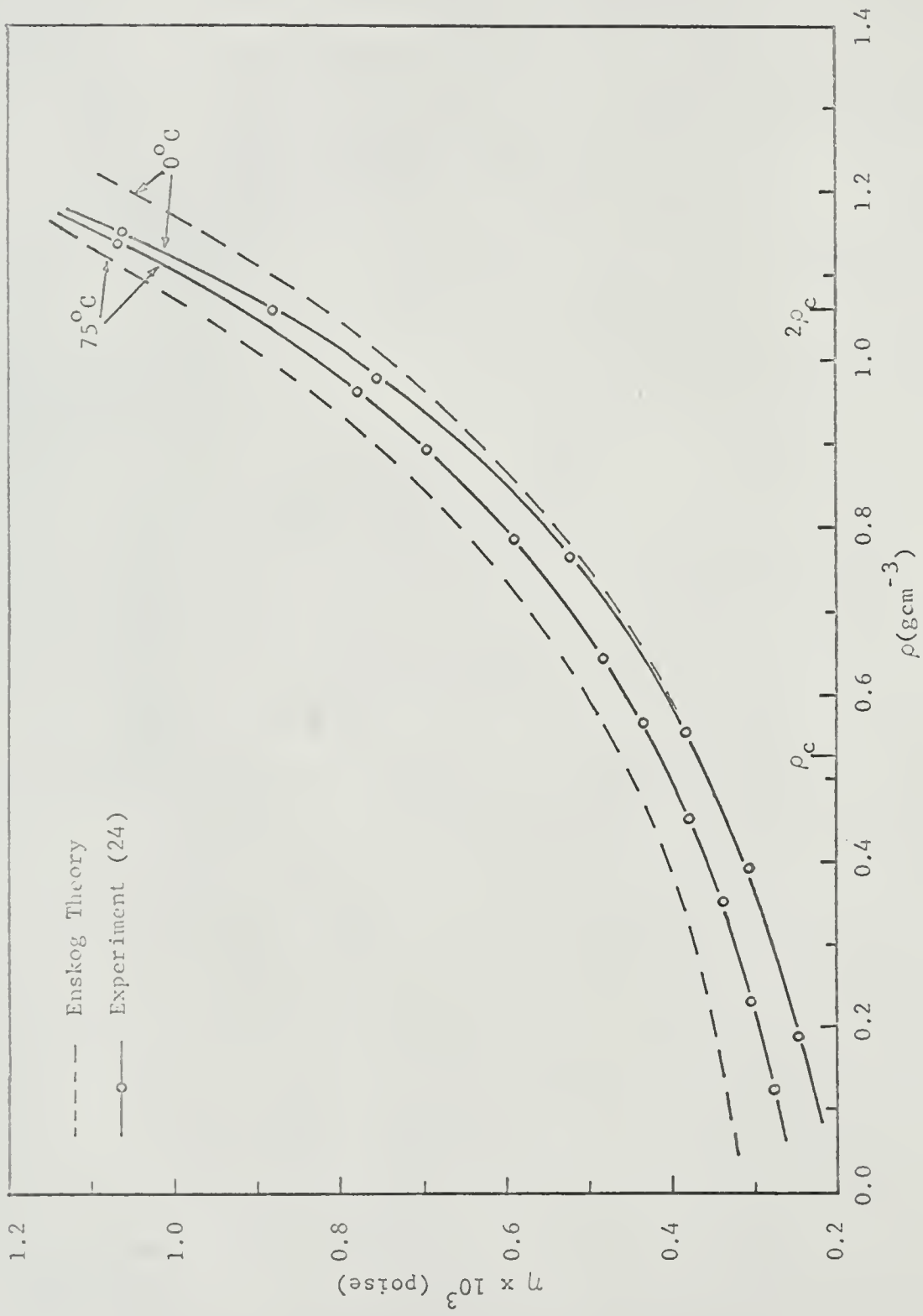


Figure 1.3. Theoretical and Experimental Viscosity of Argon - Enskog Theory.

densities up to about 0.8 g/cc. At higher densities the theory fails to predict the correct density dependence. As can be seen in Figure 1.3, the Enskog theory does not predict the correct temperature dependence. Dymond and Alder (25) recently modified the Enskog theory by using temperature dependent rigid sphere diameters obtained from the Van der Waals equation of state. With this modification, the theoretical and experimental values of viscosity are shown in Figure 1.4. The predicted temperature dependence is found to improve considerably; however the theory still fails to predict the density dependence at densities above 0.8 g/cc.

#### 1.4 Activation and Free Volume Theories

An activation theory for liquid transport properties was first proposed by Eyring (26). This type of theory assumes that a molecule spends a large fraction of its time oscillating about an equilibrium position in a cell, and only occasionally does it leave one cell to take up position in a neighboring vacant cell. Transport of mass and momentum are assumed to occur during such molecular transitions. Later modifications to Eyring's original theory have included the introduction of the concept of the fluctuating free volume. These theories are discussed in detail in Chapter 2. The free volume theories apply only at densities above approximately twice the critical value.

Horrocks and McLaughlin (27) applied the activation and free volume theory to the thermal conductivity. They assumed a face-centered-cubic lattice structure for the liquid and that transfer of thermal energy down the temperature gradient was due to two causes:

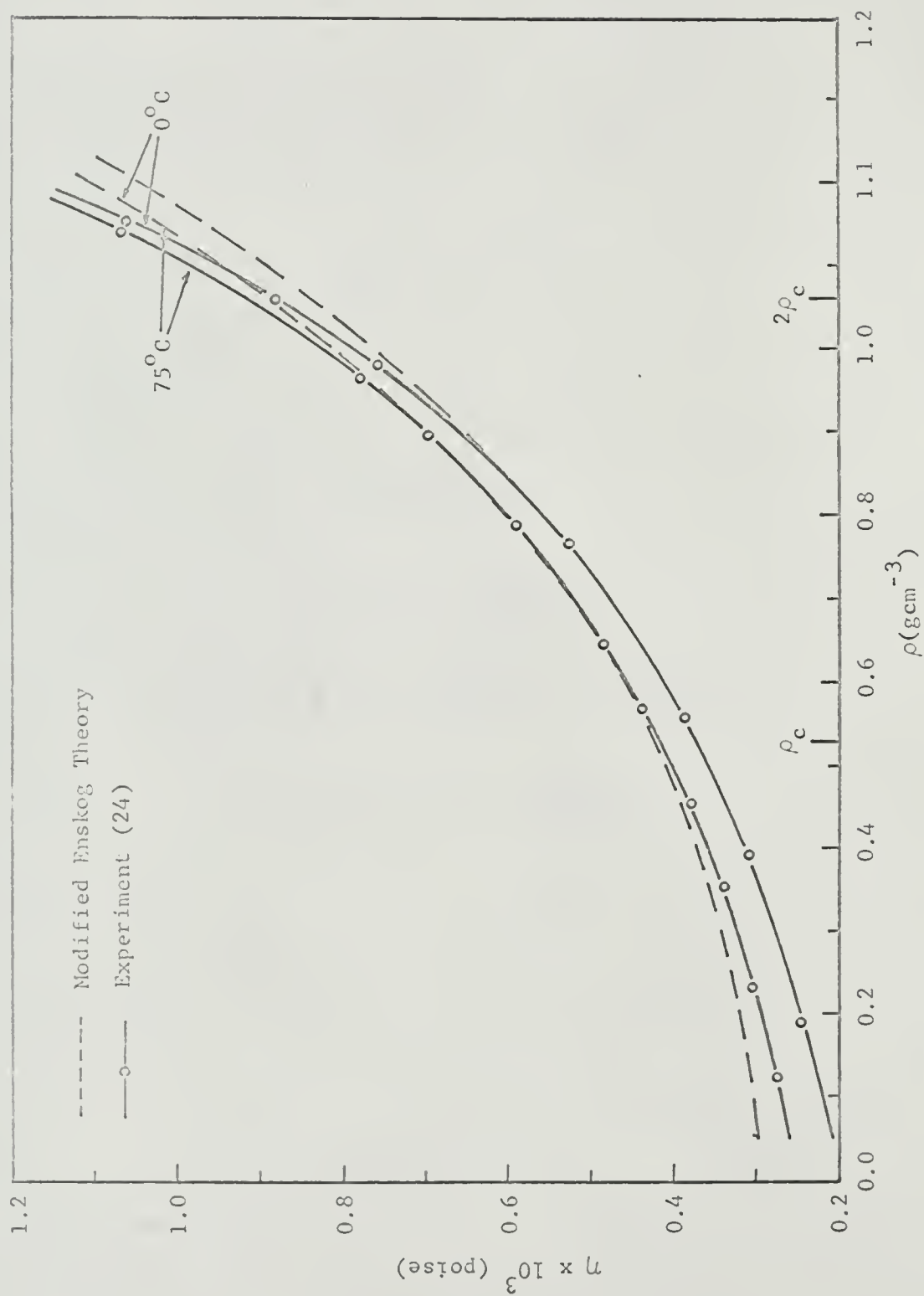


Figure 1.4. Theoretical and Experimental Viscosity of Argon - Modified Enskog Theory.

the actual transit of a molecule from one lattice site to another, and that due to the collisions of an oscillating molecule with its neighbors. For liquids the contribution due to the former cause is negligible when compared with that of the latter. The frequency of oscillation is determined by the molecular mass and the intermolecular force. Their theory has been tested for a number of simple liquids and the agreement between theory and experiment is often within 20%. Calculated and experimental thermal conductivities of a number of liquids are compared in Figure 1.5.

### 1.5 The Correspondence Principle

The principle of corresponding states has been found very useful in the calculation of equilibrium properties of dense gases and liquids (28). However very few studies have been made of its application to transport properties of dense gases and liquids. As the principle of corresponding states will be discussed in great detail in later chapters it will not be discussed further here.

### 1.6 Empirical Correlations

A very good review of the purely empirical methods of estimating transport coefficients is given in a new book by Reid and Sherwood (29). These methods have neither a theory nor a model to describe them. The many expressions proposed usually contain one or more empirical parameters or constants which are said to characterize the structure or properties of the molecules; in most cases these parameters have to be supplied by the authors of the correlation. A typical example of these correlations is Souder's method for estimating liquid viscosity, which is one of the few empirical methods recommended by Reid and Sherwood.

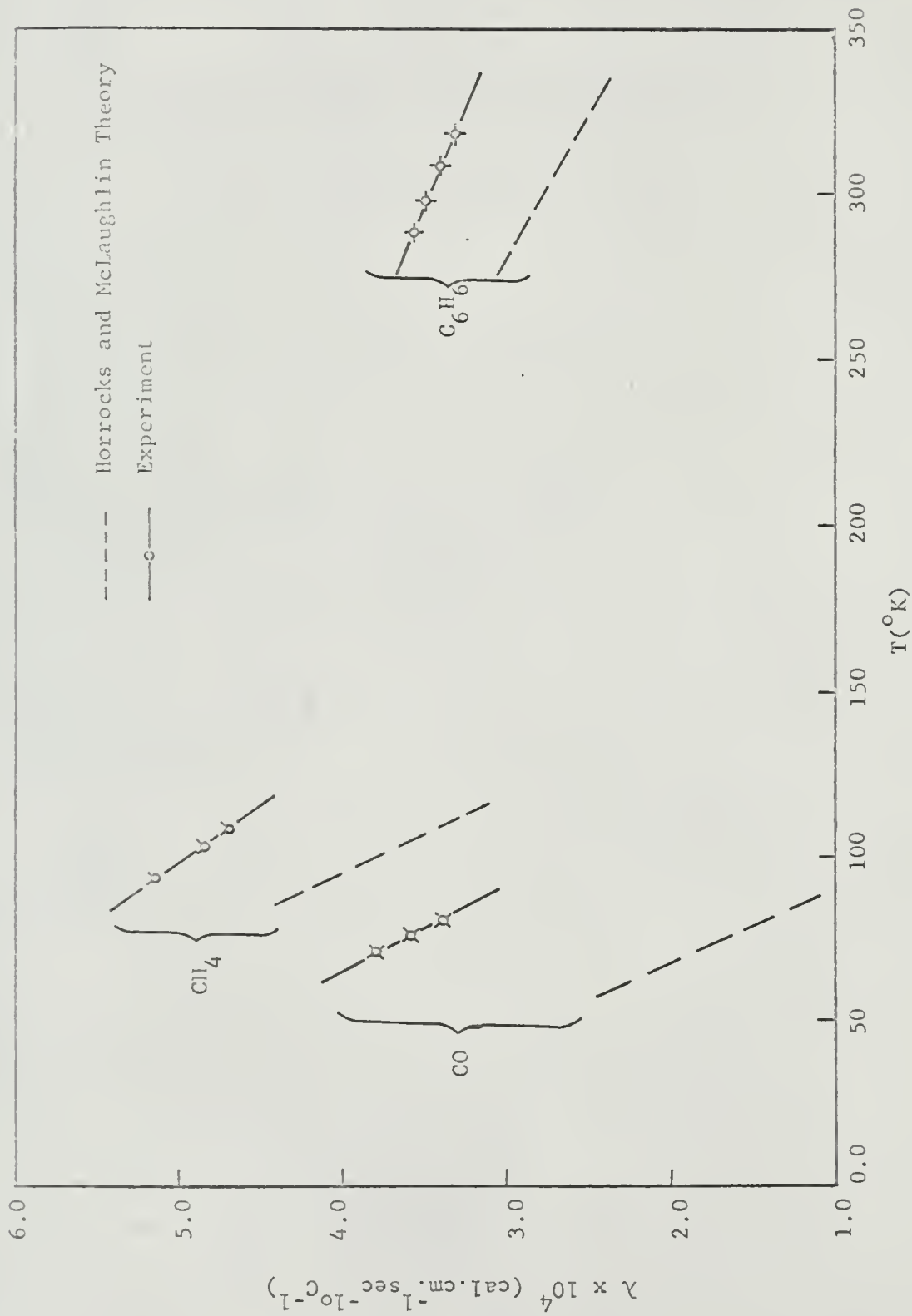


Figure 1.5. Theoretical and Experimental Thermal Conductivity - Horrocks and McLaughlin Theory.



Souder's equation is

$$\log(\log 10\eta) = \frac{I_1}{M} \rho - 2.9 \quad (1.22)$$

where  $\eta$  = liquid viscosity, centipoise

$\rho$  = liquid density, gcm.<sup>-3</sup>

$I_1$  = viscosity constant calculated from atomic and structural constants supplied by the author

$M$  = molecular weight

The results yielded by such methods are usually not very satisfactory. In spite of the author's claim that viscosity predictions are within 20%, errors are often greater than this. Thus the equation predicts a viscosity for acetic acid at 40°C that is 36% too low (29). Similar empirical expressions are also available for liquid thermal conductivity and self-diffusion coefficient; the discrepancies between these equations and experimental data are of a similar order to that of the viscosity correlations.

Among the empirical correlations, those based on residual-viscosity concepts have received much attention (30-32). Figure 1.6 is a plot of viscosity isotherms for krypton as a function of density. At the lower densities the curves are almost parallel, and this has led a number of workers to correlate the residual viscosity  $\eta - \eta_0$  with density. The general form of this correlation is

$$\eta - \eta_0 = f_1(\rho) \quad (1.23)$$

where  $f_1$  is a function of density only and  $\eta_0$  is the dilute gas viscosity. However, as can be seen in Figure 1.6, the isotherms

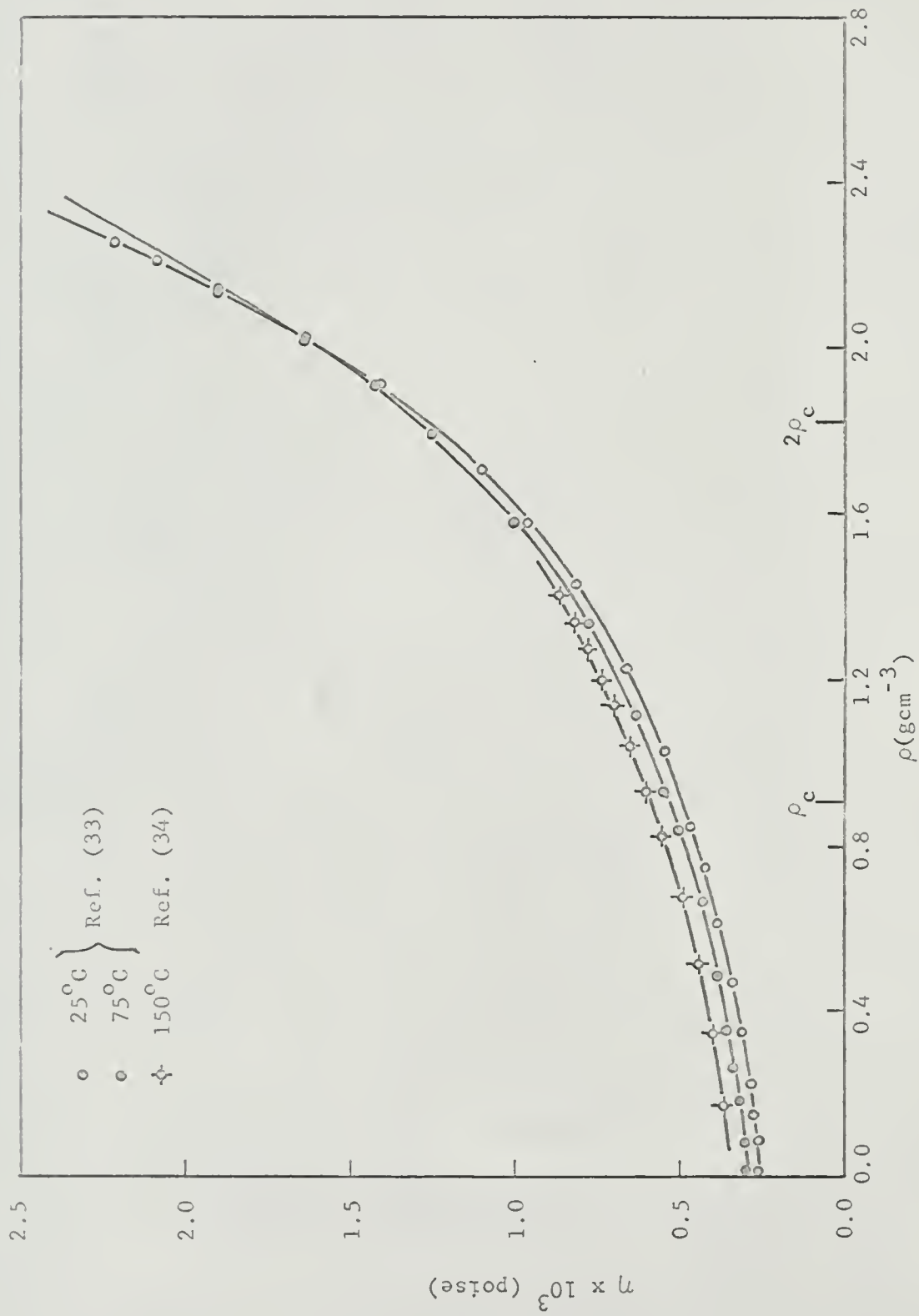


Figure 1.6. Viscosity Isotherms of Krypton as Functions of Density.

intersect at higher densities, so that such correlations are not valid over the whole density range. The intersection occurs at densities of about twice the critical value. Above this density value the free volume theory is found to work well.

### 1.7 Summary

Of the different approaches discussed above, the time correlation function theory and the kinetic theory of liquids are the most rigorous and correct descriptions of transport processes in dense fluids. In their present stage of development, however, they offer little immediate prospect of yielding methods of predicting transport properties for fluids of interest to chemical engineers.

The Enskog dense gas theory provides good results for dense gases, but fails at densities a little above the critical value. For the lower densities quite good results may also be obtained from empirical equations, such as those employing the residual viscosity concept.

At present a particular need exists for satisfactory methods of predicting transport properties for fluids at densities well above the critical, that is in the normal liquid density region. Toward this end two approaches are examined in detail in this dissertation. The free volume theory is first studied, and examined as a framework for developing predictive corresponding states relations for simple fluids. Although such a model lacks the desirable rigor present in the formal theories, it has the considerable advantage of being solvable, and suggests ways in which expressions may be obtained for mixtures. Chapter 2 briefly reviews previous work on free volume theories, and

Chapters 3 and 4 contain the new contributions to the theory.

The second approach consists of the development of corresponding states relationships directly from the time correlation function theory. The correspondence principle is particularly valuable when based on the rigorous statistical mechanical approach, but no serious attempt to apply the principle to dense fluid transport properties seems to have been made previously. This approach is examined in detail in Chapters 5 and 6.

## CHAPTER 2

### PREVIOUS WORK ON ACTIVATION AND FREE VOLUME THEORIES

Because of the present difficulties associated with developing a rigorous kinetic theory of dense fluids analogous to that available for dilute gases, considerable attention has been given to simplified models of the liquid state. Assumptions are introduced in the initial stages of the development, an attempt being made to obtain a model which incorporates the essential features of real liquids, but which is still solvable. Such attempts are exemplified by the activation and free volume theories for liquid transport properties.

Eyring (26) may be considered a pioneer in the development of activation and free volume theories for liquid transport properties. In Eyring's original approach the equilibrium positions of molecules in a liquid were considered to be on a regular lattice similar to the crystal lattice in a solid. The transport of mass and momentum occurs as a result of a molecule jumping from one equilibrium lattice site onto a vacant neighboring site. In order to make such a jump a molecule is required to have the necessary activation energy to overcome the minimum energy barrier separating two adjacent sites, and at the same time a vacant site must be available. Using this model Eyring obtained the following expressions for liquid viscosity and self-diffusivity by making use of the absolute reaction rate theory:

$$\eta = \frac{1}{2\sqrt{3}} (2\pi mkT)^{1/2} \frac{1}{q_f} e^{e_o/kT} \quad (2.1)$$

$$D = \frac{1^2 kT}{(2\pi mkT)^{1/2} q_f^{1/3}} e^{-e_o/kT} \quad (2.2)$$

More recently Weymann (35,36) used a statistical mechanical approach, and arrived at expressions very similar to those of Eyring. In his derivation of the equations for transport properties, Weymann gave a clearer picture of the physical model used and of the significance of the activation energy. Moreover his approach suggests a possible extension to liquid mixtures. Weymann also derived an expression in which the probability of hole formation is related to the volume and energy needed to form a hole. The equations obtained by Weymann for viscosity and self-diffusion coefficient are:

$$\eta = \frac{3}{4\chi_h} \left( \frac{1}{1_v^{1/3}} \right) (2\pi mkT)^{1/2} e^{e_o/kT} \quad (2.3)$$

$$D = \frac{2\chi_h}{3} \left( \frac{2kT}{\pi m} \right)^{1/2} e^{-e_o/kT} \quad (2.4)$$

where  $\chi_h$  is the probability of hole formation.

Eyring's activation theory was modified by McLaughlin (37) by introducing the concept of the probability of hole formation, as was done by Weymann. In his treatment, he assumed a face-centered-cubic lattice for the liquid. The most important modification made by McLaughlin was the attempt to relate the activation energy and energy of hole formation to the intermolecular forces by means of the Lennard-Jones and Devonshire cell theory of liquids. A similar expression for liquid viscosity was also obtained by Majumdar (38)

using the tunnel model of Barker (39) in place of the Lennard-Jones and Devonshire cell model.

The Eyring and Weymann theories yield good results for the viscosity of Arrhenius liquids (ones whose viscosity varies with temperature according to an equation of the type  $\ln \eta = C_a + B_a/T$ ), but cannot account for non-Arrhenius liquid behavior. In order to overcome this deficiency Doolittle (40-42) proposed empirical expressions which related liquid transport properties to the free volume, defined by

$$v_f = v - v_o \quad (2.5)$$

where  $v_o$  is the hard-core volume of the molecule. His free volume equations were placed on more solid theoretical grounds by Cohen and Turnbull (43,44) who derived them by a statistical mechanical method. They assumed that a molecule moves about in a cell in a gas-like manner, while the free volume available to each molecule fluctuates with time. A molecule is able to jump into a neighboring cell only if a free volume of a size greater than some minimum value  $v_o$  is available. They obtained the following expressions for the viscosity and self-diffusion coefficient:

$$\eta = \frac{1}{3\pi a^*} \left( \frac{mkT}{3} \right)^{1/2} \exp \left( - \frac{\gamma v_o}{v_f} \right) \quad (2.6)$$

$$D = g_1 a^* \left( \frac{3kT}{m} \right)^{1/2} \exp \left( - \frac{\gamma v_o}{v_f} \right) \quad (2.7)$$

The term "free volume" in these theories has a different



meaning from that implied in thermodynamic free volume theories. The theories of Doolittle and Cohen and Turnbull assumed the molecules to behave as hard spheres; the free volume referred to here is the space in the fluid unoccupied by the hard spheres themselves. The average free volume per molecule is defined as  $v - v_o$ , where  $v = V/N$ . The free volume theory of these authors describes the viscosity behavior at atmospheric pressure, but fails to predict the temperature dependence of viscosity at constant volume.

Recently, Macedo and Litovitz (45) proposed expressions for viscosity and self-diffusion coefficient in which the hole probability in Weymann's equations was replaced by the free volume expression obtained by Cohen and Turnbull. Molecular transport is assumed to occur if a molecule has sufficient energy,  $e_v$  to overcome intermolecular forces with its neighbors, and at the same time it has a free volume greater than the minimum free volume  $v_o$  needed for a jump to occur. The equations proposed for viscosity and self-diffusion coefficient are

$$\eta = A \exp \left( \frac{\gamma V_o}{V - V_o} \right) \exp \left( \frac{E_v}{RT} \right) \quad (2.8)$$

$$D = B \exp \left( - \frac{\gamma V_o}{V - V_o} \right) \exp \left( - \frac{E_v}{RT} \right) \quad (2.9)$$

By treating  $V_o$  and  $E_v$  as empirical constants Macedo and Litovitz have shown that equation (2.8) describes the viscosity behavior of a number of liquids over a range of temperature. Chung (46) has presented an elegant statistical mechanical derivation of the equation of



Macedo and Litovitz. His derivation is presented in Appendix 1.

Macedo and Litovitz assume the pre-exponential factor A in equation (2.8) to be proportional to temperature T although most other workers predict a temperature dependence of  $T^{1/2}$ . Both types of temperature dependence of the pre-exponential factor have been tested in this work, and experimental results seem to give better agreement with theory when a temperature dependence of  $T^{1/2}$  is used. Thus throughout this work the pre-exponential factors A and B are assumed to be proportional to  $T^{1/2}$ . Thus equations (2.8) and (2.9) may be rewritten as

$$\frac{\eta}{T^{1/2}} = A_o \exp \left( \frac{V_o}{V - V_o} \right) \exp \left( \frac{E_v}{RT} \right) \quad (2.10)$$

$$\frac{D}{T^{1/2}} = B_o \exp \left( - \frac{V_o}{V - V_o} \right) \exp \left( - \frac{E_v}{RT} \right) \quad (2.11)$$

where

$$A_o = \frac{A}{T^{1/2}}$$

and

$$B_o = \frac{B}{T^{1/2}}$$

Macedo and Litovitz original equations contain a constant factor  $\gamma$  which was introduced to account for the overlapping of free volumes. In the early part of this work, the constant  $\gamma$  was evaluated for a number of molecules and was found to be close to unity. This factor will therefore not be included in the equations of viscosity and diffusivity.

## CHAPTER 3

### IMPROVED FREE VOLUME THEORY

The viscosity equation (2.8) has been tested by Macedo and Litovitz (45) for a variety of liquids and by Kaelble (47) for polymeric substances. They treated the pre-exponential factor  $A_0$ , the activation energy  $E_v$  and the minimum free volume  $V_0$  as adjustable parameters characteristic of the substance considered. Equation (2.8) was found to describe the viscosity behavior of the substances tested by these workers moderately well. On the other hand, Naghizadeh and Rice (18) tested the theory for the self-diffusivity of simple fluids (such as the inert gases) and found that the agreement between theory and experiment was poor, especially in the high density region.

If  $V_0$  is a constant, as assumed by Macedo and Litovitz, differentiation of equation (2.10) with respect to  $1/T$  at constant volume (i.e. constant density) yields

$$\left[ \frac{\partial \ln(\eta/T^{1/2})}{\partial (1/T)} \right]_V = \frac{E_v}{R} \quad (3.1)$$

$E_v$  represents the minimum energy required by a molecule to overcome intermolecular forces in making a jump and was also assumed constant by Macedo and Litovitz. Therefore equation (3.1) predicts that a plot of  $\ln(\eta/T^{1/2})$  versus reciprocal temperature at constant volume should give a series of parallel straight lines. For a variety of nonpolar and slightly polar liquids over a moderate density and temperature range such a plot produces straight lines, but the slopes

of the lines vary with volume. Moreover, when the results are plotted over a wide temperature range nonlinearity becomes apparent. Such nonlinearity is particularly marked for fluids composed of simple molecules. This is illustrated in Figures 3.1 and 3.2 for argon and nitrogen, for which data are available at constant volume over wide ranges of temperature and density.

From the above discussion it is apparent that the equations as used by Macedo and Litovitz do not correctly predict qualitatively the effect of temperature and volume on the viscosity, especially for simple fluids. In addition, extensive experimental viscosity data are needed for each fluid in order to fit the adjustable parameters  $A_0$ ,  $E_v$  and  $V_0$ ; when used in this way their equation is no more than an empirical correlation.

In this chapter the physical significance of the parameters  $E_v$  and  $V_0$  is examined in the light of the theory, and their dependence on molecular type, temperature and volume is discussed. Interpretation of these quantities on the molecular level suggests corresponding states relationships which may be used to predict the parameters. The improved theory also explains why the theory of Macedo and Litovitz fails for simple fluids.

### 3.1 Temperature Dependence of $V_0$

The parameter  $V_0$  of equations (2.10) and (2.11) represents the minimum free volume that must be available before a jump may occur. If the molecules may be treated as rigid spheres, as in the smoothed potential cell model of Prigogine (50), the free volume is independent

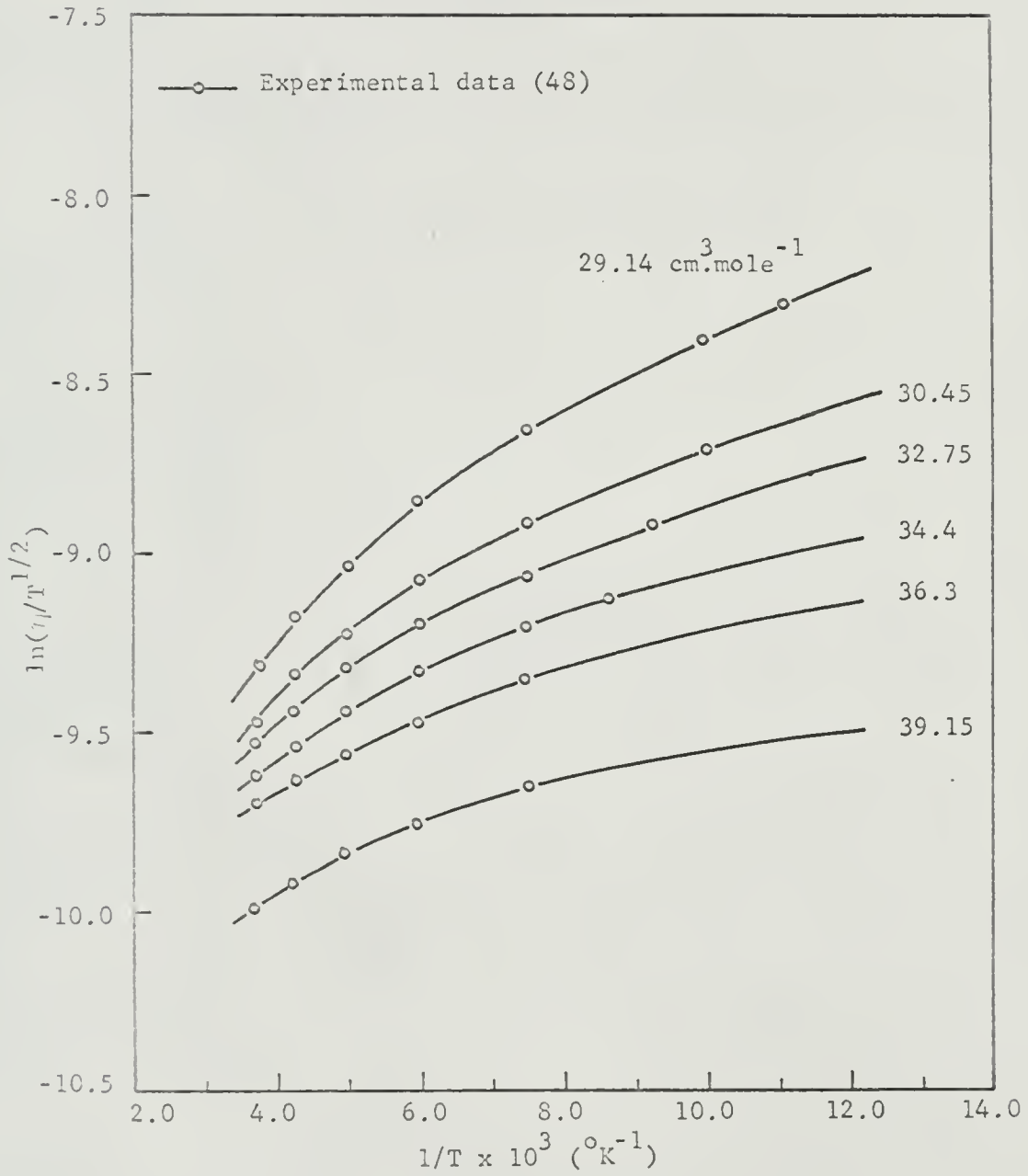


Figure 3.1. Viscosity of Argon.

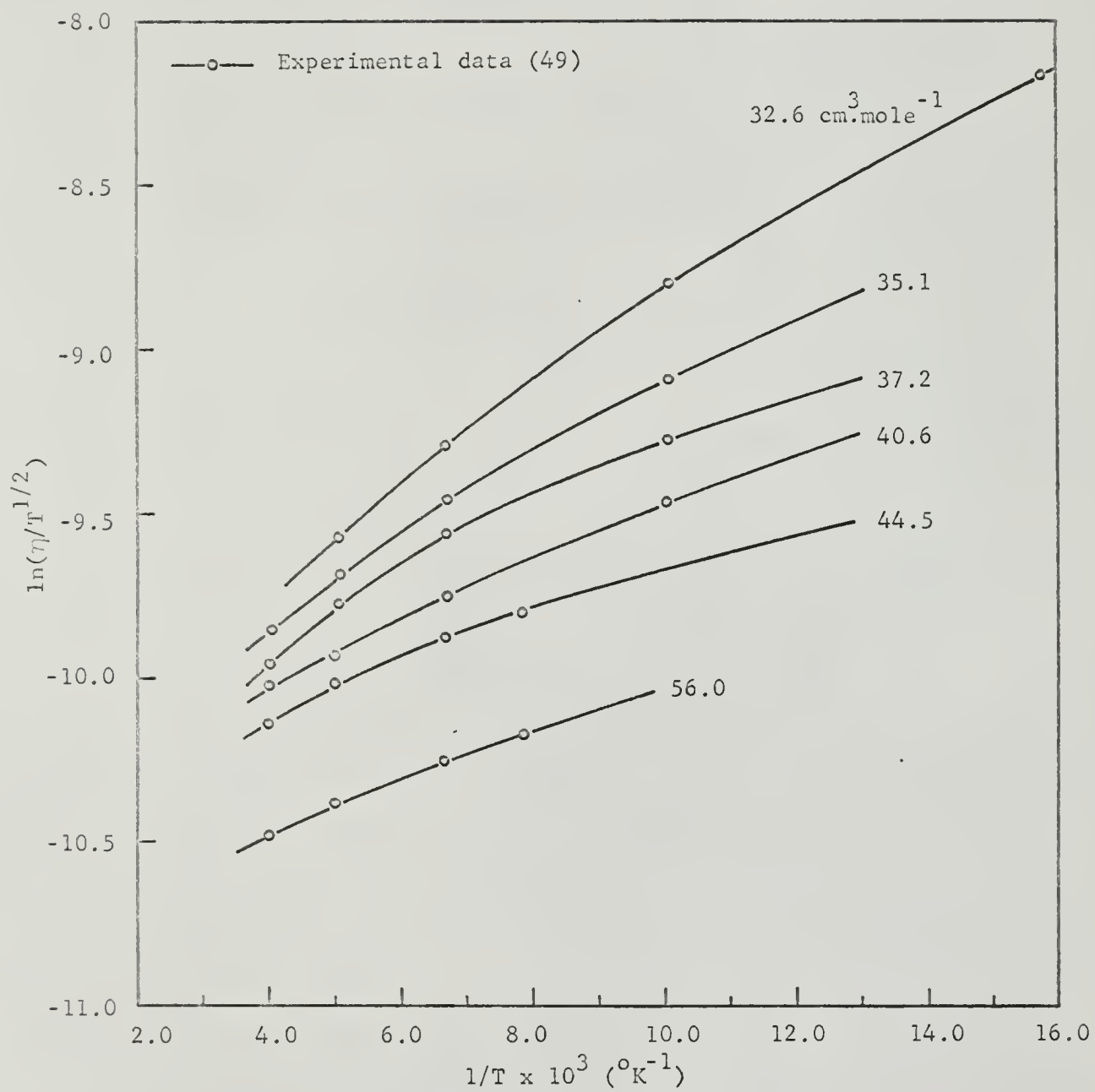


Figure 3.2. Viscosity of Nitrogen.

of the temperature at constant volume, and  $V_0$  should therefore be a constant for a particular molecule, independent of temperature and density. Macedo and Litovitz (45) assumed this to be the case for all molecules treated by them.

For more realistic potential models one would expect  $V_0$  to decrease somewhat with increasing temperature, since as temperature rises the average kinetic energy of the molecules increases, and molecules are thus able to approach each other more closely. According to such a viewpoint  $V_0$  should not be affected by the density at constant temperature. The extent to which this parameter depends on temperature will be determined largely by the repulsive portion of the intermolecular potential energy curve. Since this part of the curve rises less steeply for simple molecules than for more complex polyatomic molecules, one would expect the effect of varying  $V_0$  to be most evident for the simpler molecules.

To obtain a general expression describing the temperature dependence of  $V_0$ , a  $[6,n]$  pair potential energy function is assumed. Thus

$$u = \epsilon K_1 \left[ \left( \frac{\sigma}{r} \right)^n - \left( \frac{\sigma}{r} \right)^6 \right] \quad (3.2)$$

where

$$K_1 = \left( \frac{n}{n-6} \right) \left( \frac{n}{6} \right)^{6/(n-6)}$$

The parameter  $n$  indicates the steepness of the repulsive part of the curve; for small molecules such as the inert gases  $n$  is close to 12, whereas for more complex molecules the best values of  $n$  is 28 or

higher.

For a group of roughly spherical molecules  $V_o$  may be assumed to be proportional to the cube of the molecular "diameter." An estimate of the variation of the molecular diameter (and hence  $V_o$ ) with temperature may be obtained by equating the average kinetic energy of a two-particle system to the potential energy of the system at the distance of closest approach,  $d$ :

$$3kT = \epsilon K_1 \left[ \left( \frac{\sigma}{d} \right)^n - \left( \frac{\sigma}{d} \right)^6 \right] \quad (3.3)$$

or, in reduced form

$$3T^* = K_1 \left[ \left( \frac{1}{v_\sigma^*} \right)^{n/3} - \left( \frac{1}{v_\sigma^*} \right)^2 \right] \quad (3.4)$$

where

$$T^* = \frac{kT}{\epsilon}$$

$$v_\sigma^* = \left( \frac{d}{\sigma} \right)^3$$

Equation (3.4) may be solved to obtain  $v_\sigma^*$  as a function of  $T^*$  for various  $n$  values. The temperature dependence of  $v_\sigma^*$  for several  $n$  values is shown in Figure 3.3. Assuming that  $V_o$  is proportional to  $d^3$ , one may write

$$V_o = \xi v_\sigma^* \quad (3.5)$$

where  $\xi$  is constant for a particular molecule,  $V_o$  at any temperature can be calculated from

$$V_o = V_o^1 \cdot \frac{v_\sigma^*}{v_\sigma^* (T^* = 1)} \quad (3.6)$$

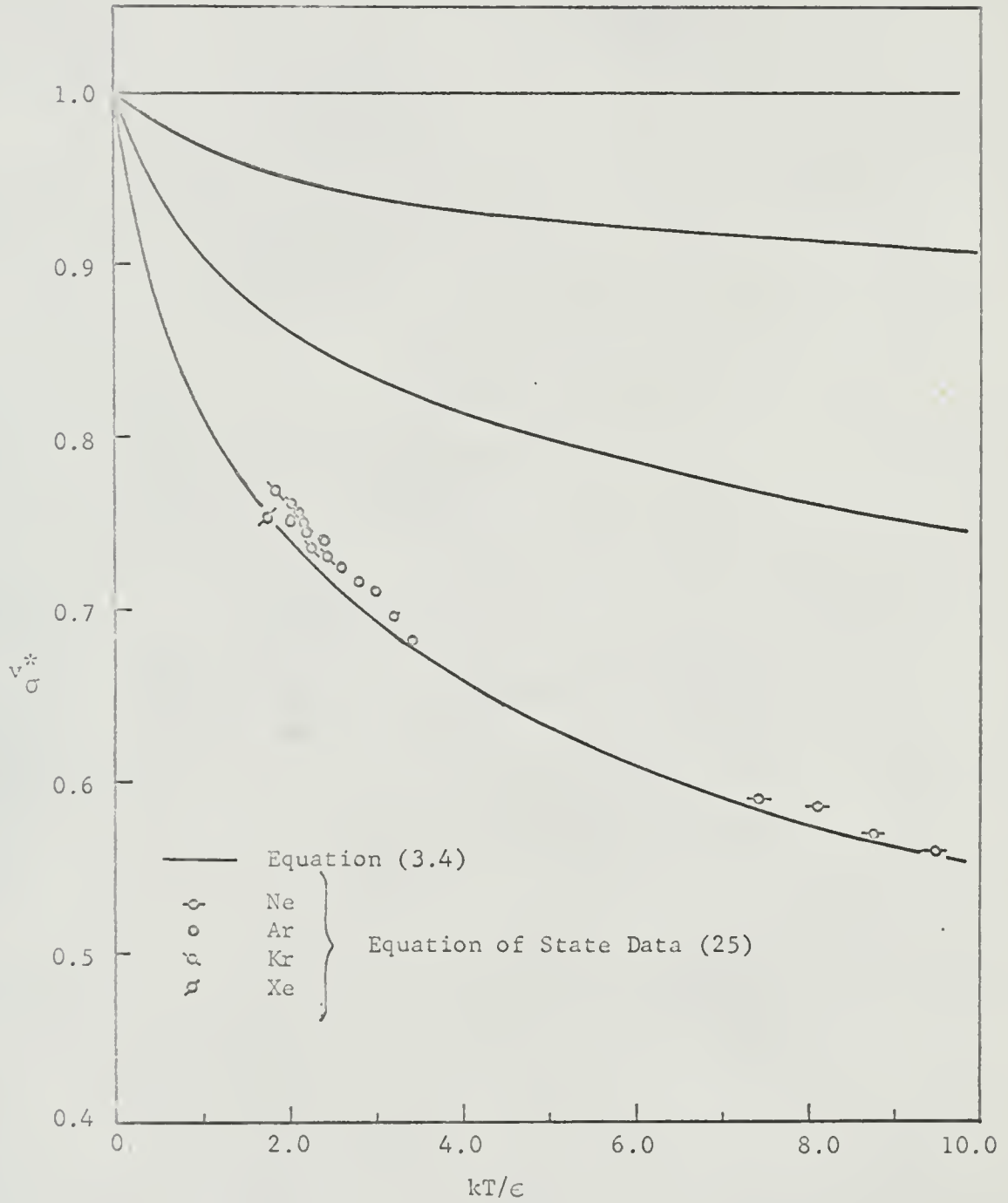


Figure 3.3. Variation of  $v_{\sigma}^*$  with  $T^*$ .



where  $V_O^1$  is the value of  $V_O$  at  $T^* = 1$ . Thus a knowledge of  $V_O^1$ , together with  $n$  and  $\epsilon$ , suffices to calculate  $V_O$  at any temperature. Some support for the above procedure is provided by values of the hard-sphere diameter calculated at various temperatures from equation of state data for inert gases by Dymond and Alder (25). These values are included in Figure 3.3, and agree well with the curve for  $n = 12$ .

With  $n = \infty$ , no temperature dependence should be observed for  $V_O$ . Under these conditions, from equation (2.10)

$$\left[ \frac{\partial \ln(\eta/T^{1/2})}{\partial (1/T)} \right]_V = \frac{E_v}{R} \quad (3.7)$$

When  $\ln(\eta/T^{1/2})$  is plotted against  $T^{-1}$  at constant volume for such nonpolar molecules as decahydronaphthalene, benzene, etc., approximately linear behavior is observed; for these molecules  $n$  is large and the variation of  $V_O$  with temperature is small. For simple molecules, such as the inert gases, for which  $n \approx 12$ , the temperature dependence is more marked, and the model predicts noticeable nonlinearity on such a plot. This is as observed experimentally, as shown in Figure 4.1 in the next chapter.

In addition to the above comments, the parameter  $V_O^1$  should be related in some way to molecular size. If  $V_O^1$  may be made dimensionless with some suitable reducing parameter, the resulting reduced minimum free volume may be quite constant for a series of similar molecules. Since free volume theories apply best at high densities, the molal volume at the melting point seems a more appropriate reducing parameter than the critical volume. Thus

$$V_o^{1*} = \frac{V_o^1}{V_m} \quad (3.8)$$

### 3.2 Volume Dependence of $E_v$

Macedo and Litovitz (45) treated the minimum activation energy  $E_v$  as an empirical constant, independent of density and temperature. However, as pointed out by Brummer (51),  $E_v$  may be expected to vary with the average intermolecular distance, and thus with density. The value of  $E_v$  becomes larger as the molal volume decreases because of the increase in repulsive intermolecular force between molecules at close separations.

From equations (2.10), (3.4) and (3.6) one may obtain

$$\frac{E_v}{R} = \lim_{T \rightarrow 0} \left[ \frac{\partial \ln(\eta/T^{1/2})}{\partial (1/T)} \right]_v \quad (3.9)$$

so that  $E_v$  may be calculated from experimental viscosity values. For more complex molecules where  $n$  is large, a plot of  $\ln(\eta/T^{1/2})$  versus  $1/T$  is found to be approximately linear, and the requirement  $T \rightarrow 0$  in equation (3.9) is less stringent. Figure 3.4 shows the volume dependence of  $E_v$  for several fluids as calculated from equation (3.9).

The activation energy arises from the motion of the jumping molecule from its initial equilibrium position through a region of higher potential energy to its final position. A model of the situation is shown in Figure 3.5 in which a molecule jumps from A to C, and passes through a region B in which it has to squeeze through a ring of  $z$  molecules. The activation energy may be written

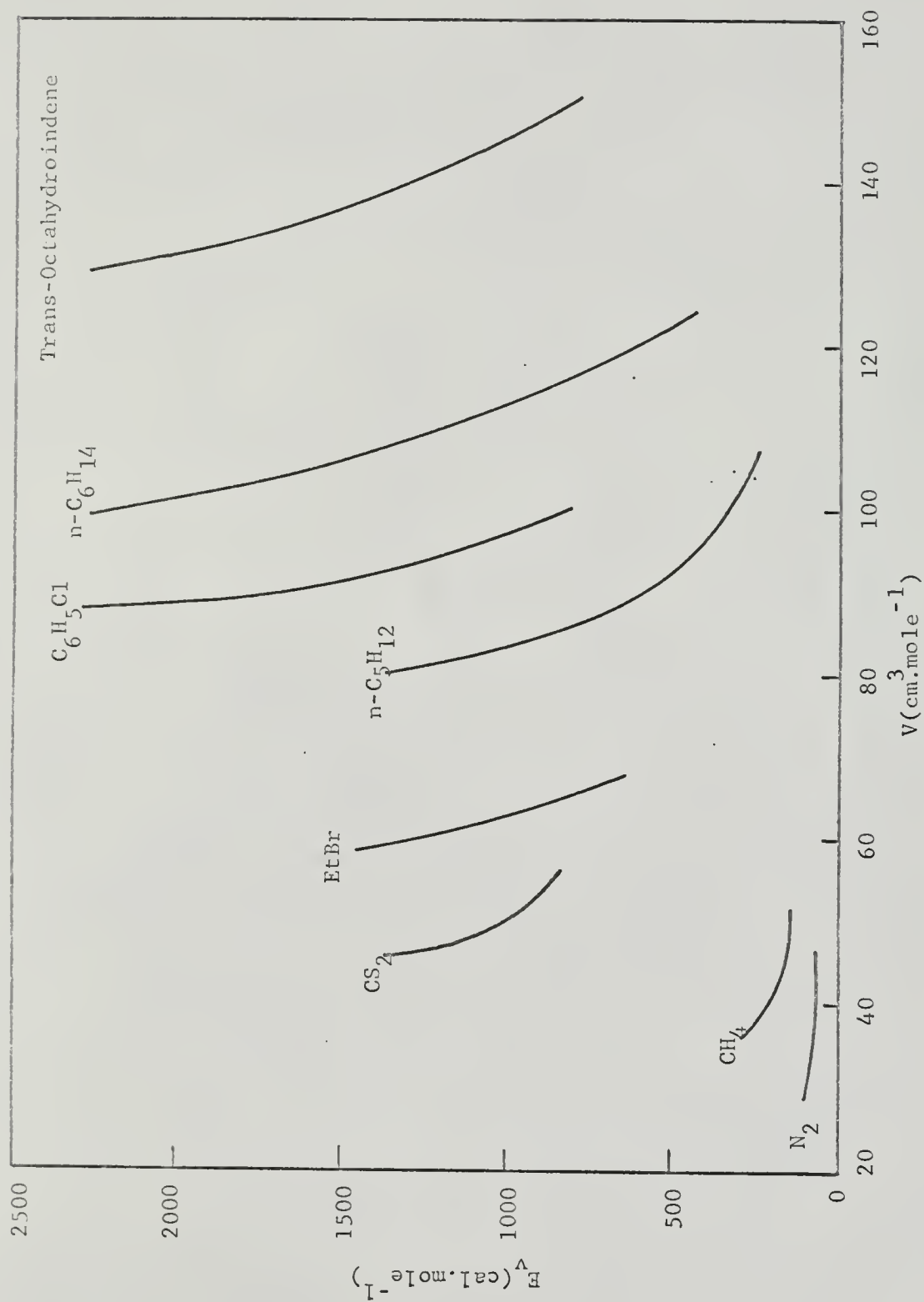


Figure 3.4. Activation Energy as a Function of Volume.

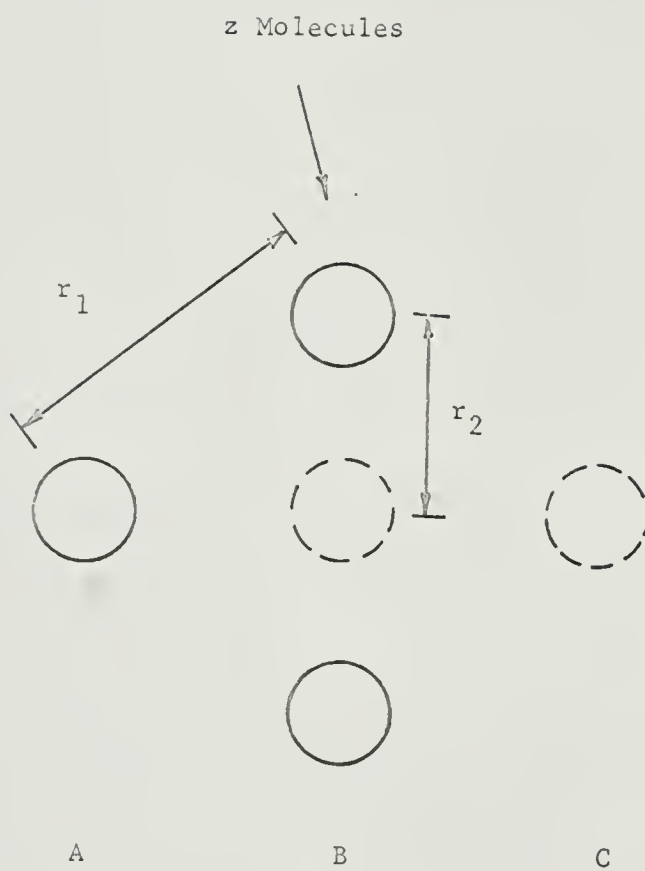


Figure 3.5. Model of a Molecular Jump.

$$\begin{aligned}
e_v &= z[u(r_2) - u(r_1)] \\
&= K_1 z \epsilon \left[ \left( \frac{\sigma}{r_2} \right)^n - \left( \frac{\sigma}{r_2} \right)^6 \right] - K_1 z \epsilon \left[ \left( \frac{\sigma}{r_1} \right)^n - \left( \frac{\sigma}{r_1} \right)^6 \right]
\end{aligned} \tag{3.10}$$

Define

$$\begin{aligned}
c_1 &= v/r_1^3 \\
c_2 &= (r_2/r_1)^3 \\
c_3 &= c_1 \sigma^3/v_m \\
c_4 &= \frac{\epsilon}{kT_m}
\end{aligned}$$

Then

$$e_v = K_1 z k T_m c_4 \left( \left[ \left( \frac{c_3 v_m}{c_2 v} \right)^{n/3} - \left( \frac{c_3 v_m}{c_2 v} \right)^2 \right] - \left[ \left( \frac{c_3 v_m}{v} \right)^{n/3} - \left( \frac{c_3 v_m}{v} \right)^2 \right] \right) \tag{3.11}$$

The parameters  $c_1$ ,  $c_2$ ,  $c_3$ ,  $c_4$  and  $n$ , the repulsive exponent should be approximately the same for a group of similar molecules and thus equation (3.11) suggests a corresponding states relation of the form

$$E_v^* = E_v^*(\tilde{V}^*) \tag{3.12}$$

where

$$E_v^* = \frac{E_v}{RT_m}$$

and

$$\tilde{V}^* = \frac{V}{V_m}$$

Figure 3.6 shows the correlations of reduced activation energy as a function of reduced molal volume for several nonpolar molecules. Good agreement is obtained at high reduced volumes, but some scatter is

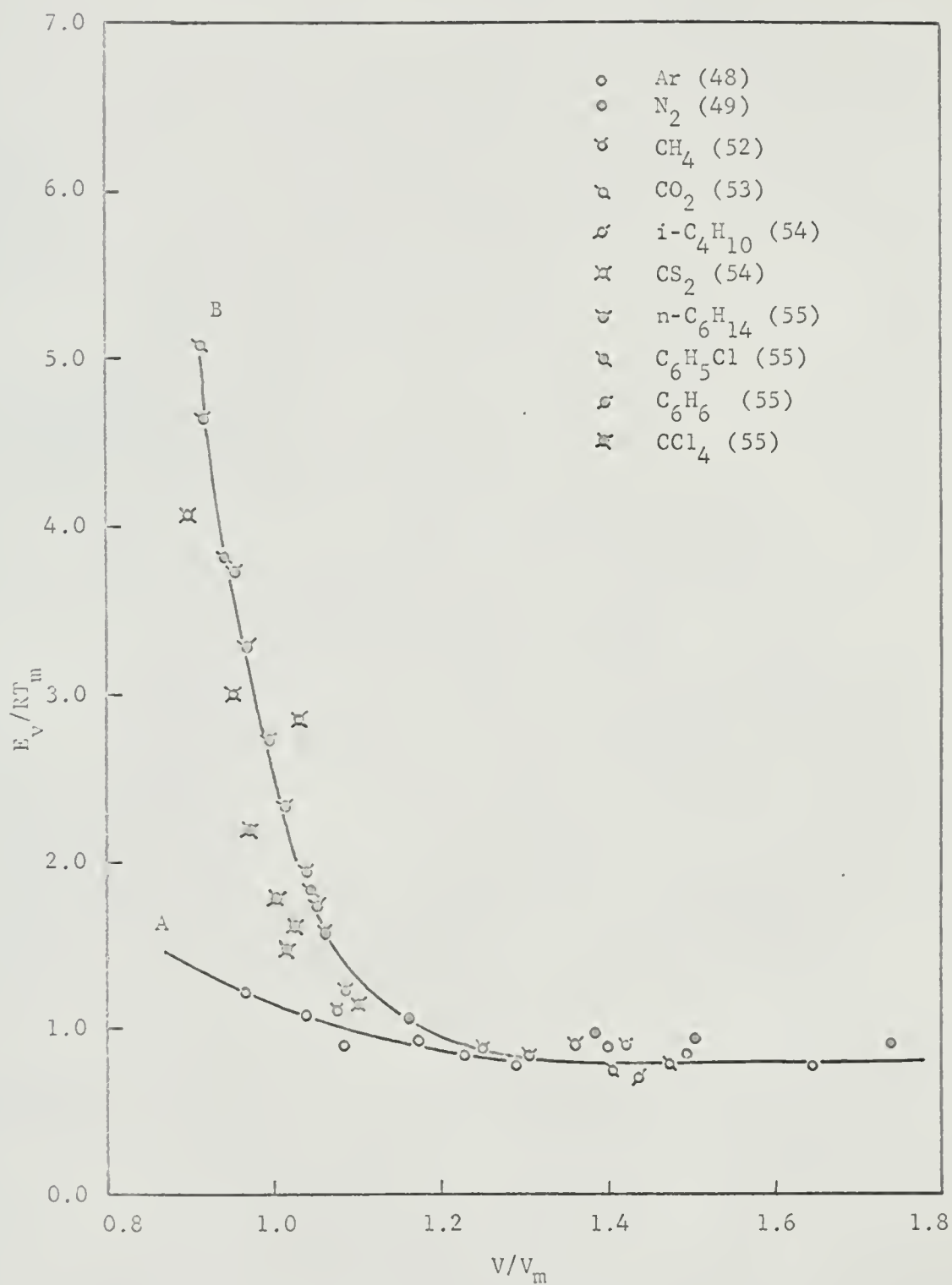


Figure 3.6. Corresponding States Correlation of Activation Energy vs. Volume.

observed at lower values of  $\tilde{V}^*$ , where the curve rises steeply. This may be attributed to differences in  $n$ , the repulsive exponent, for the molecules within the group. Thus two curves A and B are plotted in Figure 3.6. Curve A is for simple molecules obeying a Lennard-Jones [6,12] potential. Curve B shows an approximate relationship for more complex molecules which obey a potential law in which  $n$  is larger than 12. Sources of viscosity data from which values of  $E_v$  are calculated are given in Figure 3.6.

Taking into consideration the temperature dependence of  $V_o$  and the volume dependence of  $E_v$ , the modified viscosity and self-diffusion coefficient equations become:

$$\frac{\eta}{T^{1/2}} = A_o \exp \left( \frac{V_o(T)}{V - V_o(T)} \right) \exp \left( \frac{E_v(V)}{RT} \right) \quad (3.13)$$

and

$$\frac{D}{T^{1/2}} = B_o \exp \left( - \frac{V_o(T)}{V - V_o(T)} \right) \exp \left( - \frac{E_v(V)}{RT} \right) \quad (3.14)$$

## CHAPTER 4

### TEST OF IMPROVED FREE VOLUME THEORY

In order to perform a rigorous test of the theory, viscosity and self-diffusion coefficient data over a wide range of temperature and density conditions are most desirable. In this work only fluids composed of simple molecules which approximately obey the Lennard-Jones (6,12) potential law will be considered. These fluids include the inert gases and most diatomic fluids and perhaps methane, fluoromethane and tetradeuteromethane.

The only monatomic and diatomic fluids for which viscosity data over a wide range of temperature and density conditions are available seem to be argon and nitrogen. Zhadanova (48,49) has reported viscosity measurements for these fluids for experimental conditions corresponding to pressures up to several thousand atmospheres. The accuracy of the experimental argon data appears to be of the order 6% over the entire range of conditions. However, the nitrogen data are in poorer agreement with measurements of other workers, and the accuracy appears to be of the order 12-15%.

The only high pressure self-diffusivity measurements for simple liquids seem to be those of Naghizadeh and Rice (18), who reported measurements for argon, krypton, xenon and methane over a reasonable range of temperature and at pressures up to a more than one hundred atmospheres. Naghizadeh and Rice claimed that the uncertainty of their experimental data was less than 5%. However the disagreement between their argon data and those of Corbett and Wang (56) is about



12%, while their xenon data differ from those of Yen and Norberg (57) by as much as 86% and their reported methane data are about 11% higher than those of Gaven, Waugh and Stockmayer (58).

#### 4.1 Corresponding States Relationships

The following procedures were employed to test the theory for viscosity and to establish the corresponding states relationships in equations (3.8) and (3.12).

(1) The experimental data were plotted as  $\ln(\eta/T^{1/2})$  against  $T^{-1}$  at constant volume. Values of  $E_v$  were estimated at various volumes from the lines extrapolated to low temperature, since from equation (3.9)

$$\frac{E_v}{R} = \lim_{T \rightarrow 0} \left[ \frac{\partial \ln(\eta/T^{1/2})}{\partial (1/T)} \right] \quad (4.1)$$

(2) Values of the parameters  $A_0$  and  $V_O^1$  were obtained from the best fit to the viscosity data using the computer, equations (3.4) and (3.6) being used to obtain the temperature dependence of  $V_O$ .

Values of  $E_v$  for argon and nitrogen estimated by procedure (1) are included in Figure 3.6. Theoretical and experimental liquid argon viscosity values are shown in Figure 4.1. Agreement between theory and experiment is found to be within 5%. Similar agreement between theory and experiment is found for nitrogen, with  $V_O^1 = 17.0$  cc/mole and  $A_0 = 2.53 \times 10^{-5}$  poise  $(^\circ K)^{-1/2}$ , and is shown in Appendix 2. The theory provides a satisfactory fit to the data for densities above twice the critical value. Thus as can be seen in Figure 4.1 the theory fails for molal volumes of 39.15 cc/mole and above for argon. Similar behavior is also observed for the nitrogen viscosity (see Figure A2.1

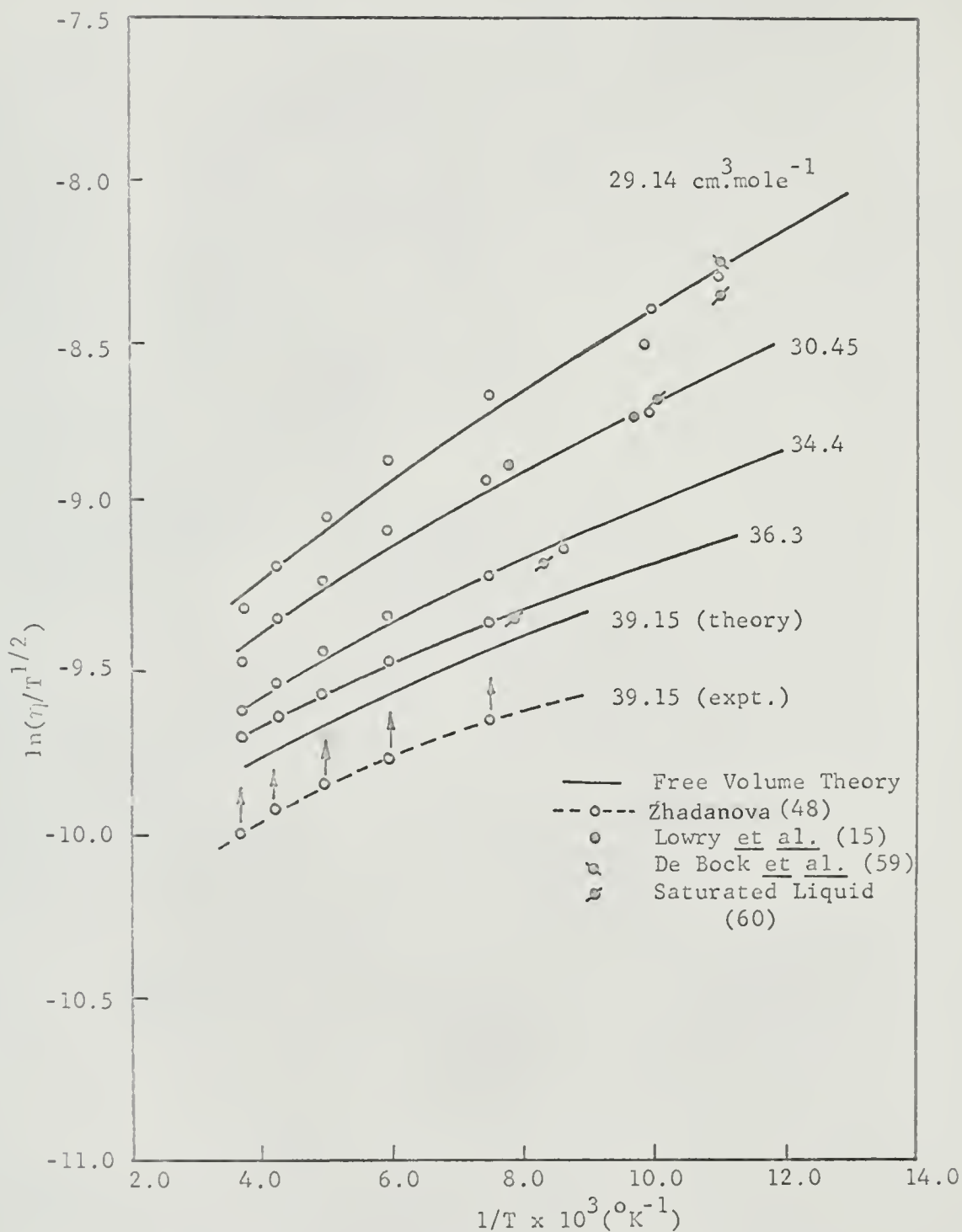


Figure 4.1. Test of Free Volume Theory for Liquid Argon Viscosity.

in Appendix 2), where the theory fails for molal volumes of 56.0 cc/mole and above. The density range in which the theory applies is sharply defined and is similar to that in which similar models for thermodynamic properties, such as the Prigogine smoothed potential model (50), apply. The theory appears to work well for temperatures below about  $1.5 T_c$ , although the temperature range in which the theory applies is less clearly defined.

The values of the parameters  $E_v$  and  $V_o^1$  found for argon and nitrogen may be used to form the basis of corresponding states correlations of these parameters as described in Chapter 3, from which viscosity and self-diffusivity values of other molecules may be predicted. The average value of the reduced minimum free volume for argon and nitrogen is 0.554, so that

$$V_o^{1*} = \frac{V_o^1}{V_m} = 0.554 \quad (4.2)$$

#### 4.2 Test of Proposed Correlations

To use equations (2.10) and (2.11) to estimate the viscosity and self-diffusion coefficient for simple molecules, values of  $V_o$  were calculated from equations (3.4), (3.6) and (4.2), assuming  $n = 12$  and taking values of  $\epsilon/k$  determined from gas viscosity data (20). Values of  $E_v$  were found using curve A of Figure 3.6. The best values of  $A_o$  were obtained by substituting experimental viscosity data in equation (2.10) for each molecule. In a similar manner, by fitting experimental self-diffusion coefficient data of each molecule into equation (2.11) the best values of  $B_o$  were obtained. Other than the viscosity data

for argon and nitrogen of Zhdanova (48, 49) and self-diffusion coefficient data of Naghizadeh and Rice (18), very few high pressure viscosity and self-diffusivity data are available. Thus most of the viscosity and self-diffusivity data used are for saturated liquids. Table 4.1 shows the viscosity data sources and ranges of temperature and density for each of the molecules studied. The different parameters which are required for the estimation of viscosity with equation (2.10) and the average percent deviation between theory and experiment are shown in Table 4.2. Tables 4.3 and 4.4 provide similar information for the self-diffusion coefficient of the molecules studied.

The average percent deviation between theory and experiment is about 6% or less for viscosity. For self-diffusion coefficient the discrepancy between experiment and theory is found to be much larger, being about 15% in most cases. The discrepancies between theory and experiment for both viscosity and self-diffusion coefficient seem to be of the same order as the accuracy of the experimental data for the liquids studied. The viscosity data of Zhdanova for nitrogen at high pressures seem to be in poor agreement with those of other workers (66), and saturated liquid viscosity data (66) were used in obtaining the  $A_0$  value given in Table 4.2 for this fluid.

Experimental and predicted viscosities for xenon and methane are compared in Figures 4.2 and 4.3 (similar plots for Ne, Kr and  $N_2$  are shown in Appendix 2). The predicted values become less reliable as density falls to values approaching  $2\rho_c$  (for methane this corresponds

TABLE 4.1

## VISCOSITY DATA SOURCES AND RANGE OF CONDITIONS

Molecule	Temperature Range (°K)	Molal Volume Range (cm. <sup>3</sup> mole <sup>-1</sup> )	Density Reference	Viscosity Reference	Number of Points
Ne	28-38	17-21	60	61, 62	7
Ar	90-270	29-39	48, 63	48, 15, 60, 59	26
Kr	115-125	34-35	64	64	4
Xe	162-323	44-54	64, 65	64, 65	7
N <sub>2</sub>	70-106	32-47	49, 66	49, 66	12
O <sub>2</sub>	81-148	27-45	64, 66	67, 68	10
CO	69-81	33-35	64, 66	64, 67	6
CH <sub>4</sub>	97-165	36-48	64, 66	64, 68, 69	8
CD <sub>4</sub>	93-115	36-38	64	64	5

TABLE 4.2

## PARAMETERS FOR VISCOSITY PREDICTION

Molecule	$\frac{1}{V_o}$ ( $\text{cm}^3 \text{mole}^{-1}$ )	$10^5 A_o$ ( $\text{poise}^\circ \text{K}^{-\frac{1}{2}}$ )	$\epsilon/k$ ( $^\circ \text{K}$ )	$T_m$ ( $^\circ \text{K}$ )	$V_m$ ( $\frac{3}{\text{cm}^3 \text{mole}^{-1}}$ )	$V_c$ ( $\frac{3}{\text{cm}^3 \text{mole}^{-1}}$ )	$\frac{A_o V_o^{2/3}}{M^{\frac{1}{2}}} \cdot 10^5$	Average % Error
Ne	8.95	2.52	35.7	24.57	16.2	41.7	3.59	2.9
Ar	15.5	2.65	124	83.2	28.0	75.2	3.87	4.7
Kr	19.0	3.10	190	116.2	34.3	92.2	3.57	0.5
Xe	24.6	3.48	229	161.2	44.3	118.8	3.80	2.5
N <sub>2</sub>	17.8	2.53	91.5	63.1	32.2	90.1	4.85	5.5
O <sub>2</sub>	13.5	3.91	113	54.8	24.3	78	5.81	5.3
CO	18.3	2.54	110	68.1	33.1	93.1	5.06	2.5
CH <sub>4</sub>	19.5	1.59	148	90.7	35.2	99	4.26	2.7
CD <sub>4</sub>	19.5	1.77	146	89.8	35.1	99	4.24	1.3

TABLE 4.3

## SELF-DIFFUSIVITY DATA SOURCES AND RANGE OF CONDITIONS

Molecule	Temperature Range (°K)	Molal Volume Range (cm. <sup>3</sup> /mole <sup>-1</sup> )	Density Reference	Viscosity Reference	Number of Points
Ar	85-110	28-31	48, 63	18, 56	16
Kr	110-160	33-41	64	18	8
Xe	168-208	43-48	64, 65	18	12
CO	69-78	33-35	64, 66, 70	71	4
CH <sub>4</sub>	91-145	35-43	64, 66	18, 58, 72	10
CF <sub>4</sub>	88-123	45-52	73	72	10

TABLE 4.4

PARAMETERS FOR SELF-DIFFUSIVITY PREDICTION

Molecule	$\frac{V_o^1}{(\text{cm}^3 \cdot \text{mole}^{-1})}$	$\frac{10^5 B_o}{(\text{cm}^2 \cdot \text{sec}^{-1} \cdot \text{OK}^{-\frac{1}{2}})}$	$\frac{\epsilon/k}{(\text{OK})}$	$\frac{T_m}{(\text{OK})}$	$\frac{V_m}{(\text{cm}^3 \cdot \text{mole}^{-1})}$	$\frac{V_c}{(\text{cm}^3 \cdot \text{mole}^{-1})}$	$\frac{B_o M^{\frac{1}{2}}}{V_m^{1/3}} \cdot 10^5$	Average % Error
Ar	15.50	1.83	124.0	83.2	28.0	75.2	3.81	15.3
Kr	19.02	1.39	190.0	116.2	34.3	92.2	3.92	17.8
Xe	24.55	1.66	229.0	161.2	44.3	118.8	5.41	14.3
CO	18.34	3.14	110.0	68.1	33.1	93.1	5.17	5.9
CH <sub>4</sub>	19.5	2.91	148.0	90.7	35.2	99.0	3.55	9.0
CF <sub>4</sub>	25.2	0.50	151.5	89.5	45.5	138.0	1.31	12.9



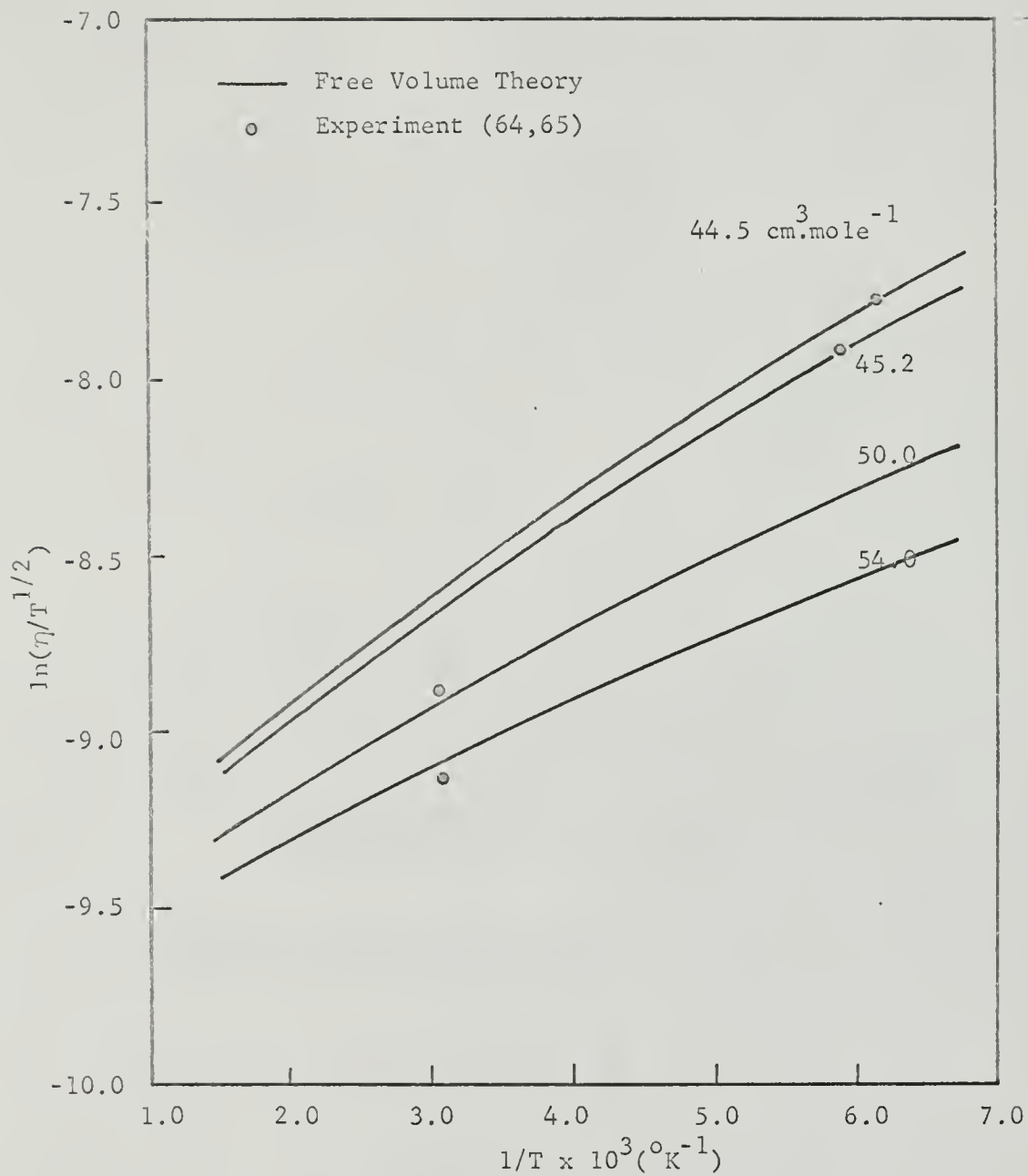


Figure 4.2. Test of Free Volume Theory for Liquid Xenon Viscosity.

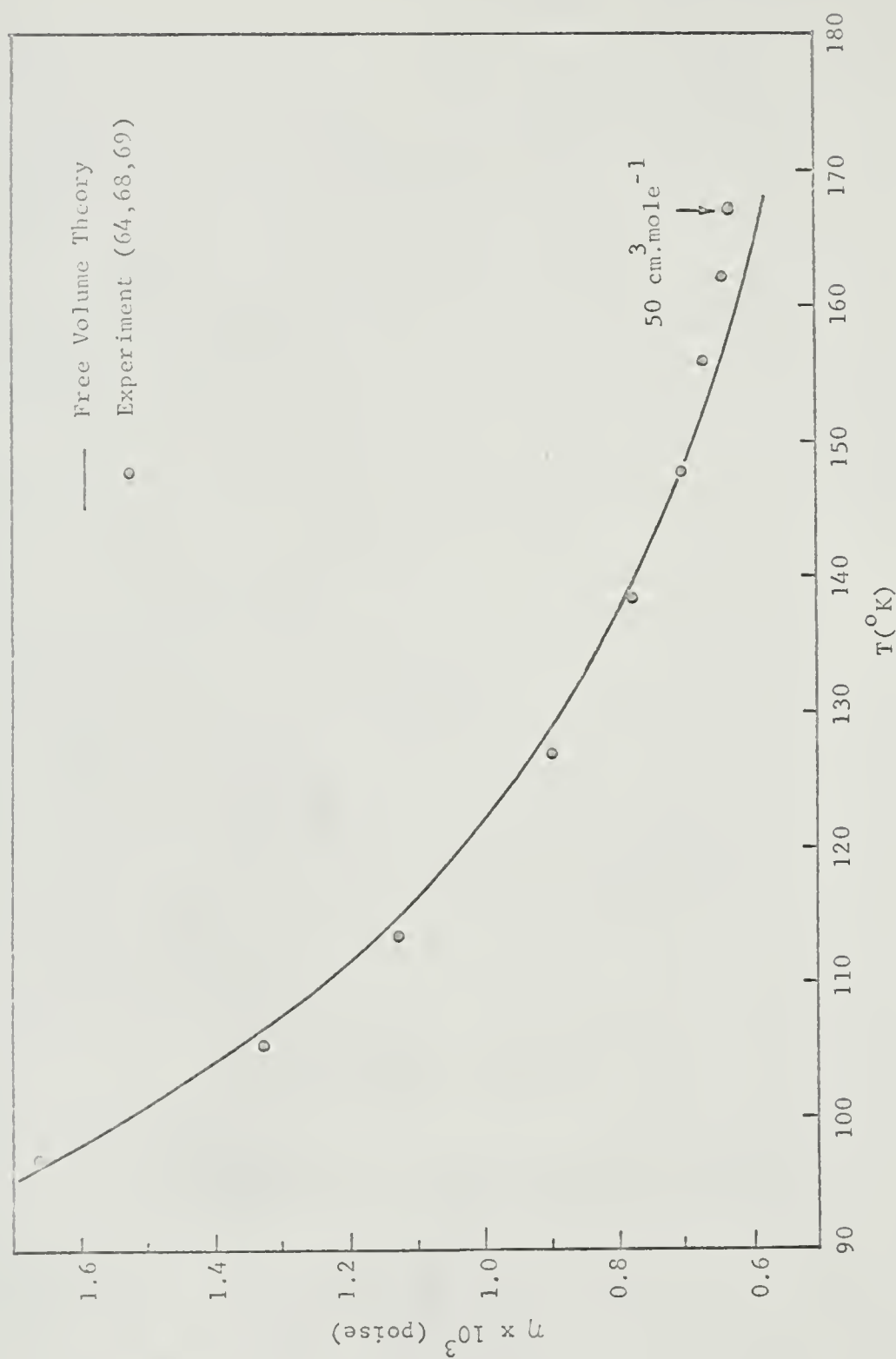


Figure 4.3. Test of Free Volume Theory for Saturated Liquid Methane Viscosity.

to  $V = 49.5$  cc/mole). Figure 4.4 compares theory and experiment for the self-diffusion coefficient of saturated liquid methane.

The expressions for the pre-exponential factors of the viscosity and self-diffusion coefficient equations of Eyring (26) and Weymann (35) suggest that the groups  $(A_0 V_m^{2/3} / M^{1/2})$  and  $(B_0 M^{1/2} / V_m^{1/3})$  may be approximately the same for different molecules. Values shown in Table 4.2 indicate that the quantity  $(A_0 V_m^{2/3} / M^{1/2})$  is approximately constant for inert gas liquids, but for the other molecules a range of values is found. Similar behavior is observed for the group  $(B_0 M^{1/2} / V_m^{1/3})$ . Apparently the expressions given for the pre-exponential factors by Eyring and Weymann are not generally valid, and cannot form the basis of successful corresponding states relationships for  $A_0$  and  $B_0$ . In general the value  $A_0$  (or  $B_0$ ) can be determined from a single experimental value of viscosity (or self-diffusivity) for a given fluid. This can then be used together with the proposed correlations for  $V_0$  and  $E_v$  to predict viscosity (or self-diffusivity) values at other temperatures and densities.

#### 4.3 Summary

By allowing for the variation of  $V_0$  with temperature it is possible to account quantitatively for the nonlinearity of constant volume plots of  $\ln(\eta/T^{1/2})$  vs.  $T^{-1}$  and  $\ln(D/T^{1/2})$  vs.  $T^{-1}$  for simple liquids. The physical model predicts a density dependence of  $E_v$ , and thus explains the variation with density of the slope of constant volume plots of  $\ln(\eta/T^{1/2})$  vs.  $T^{-1}$  and  $\ln(D/T^{1/2})$  vs.  $T^{-1}$ . With these improvements the free volume theory is able to accurately describe the viscosity and self-diffusivity behavior of liquids composed of

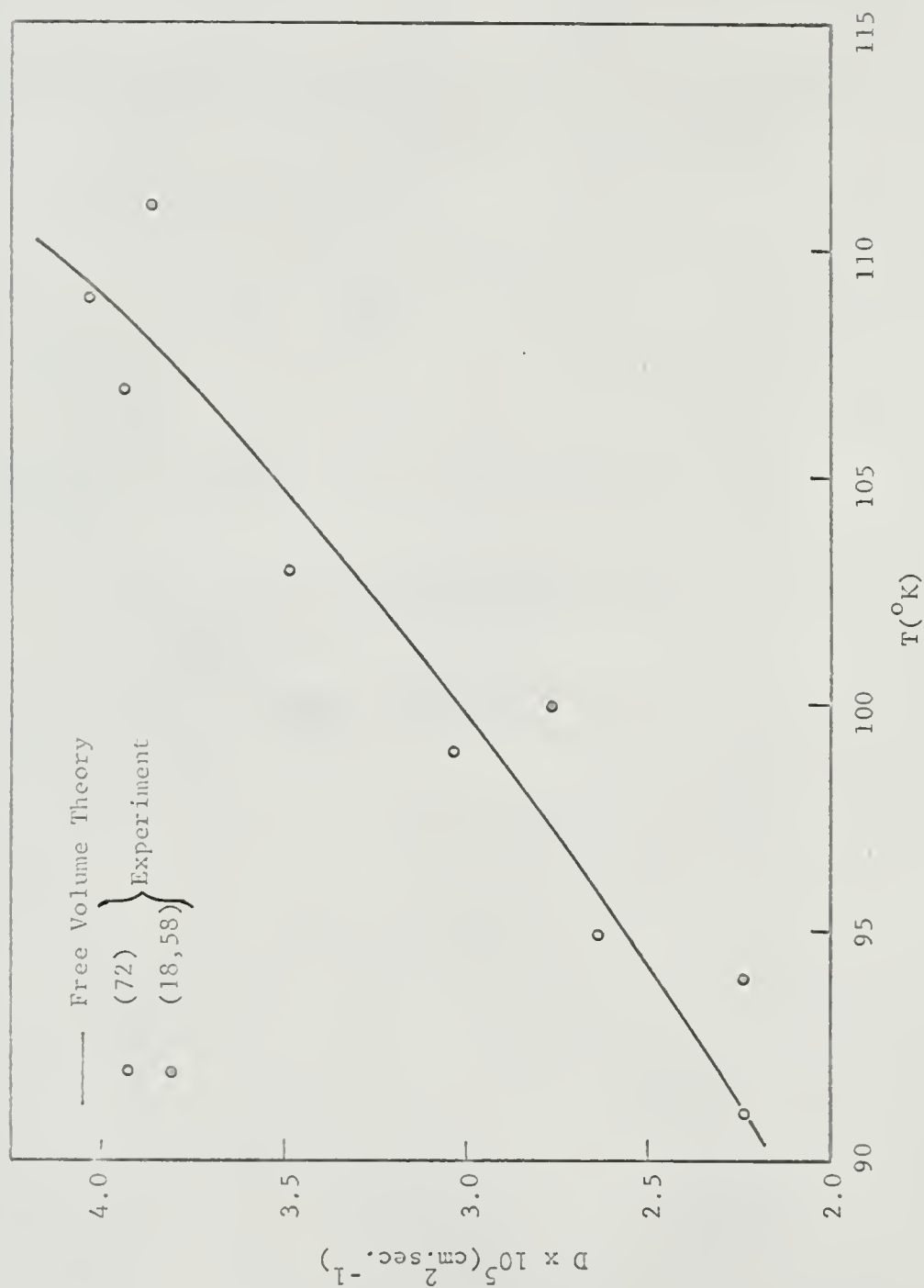


Figure 4.4. Test of Free Volume Theory for Saturated Liquid Methane Self-Diffusivity.

simple, nonpolar molecules that may be expected to approximately obey a Lennard-Jones [6,12] potential law. The theory works well at densities  $\rho > 2\rho_c$ , where other correlations fail.

The fact that both  $V_O^1$  and  $E_v$  values vary in a corresponding states way indicates that the free volume theory provides a reasonably correct picture of viscosity and self-diffusivity behavior for these liquids, and shows that the equations' success does not arise only from the availability of three adjustable parameters. The simple expressions given for  $A_O$  and  $B_O$  by Eyring and others, however, do not seem to be generally applicable.

## CHAPTER 5

### PRINCIPLE OF CORRESPONDING STATES FOR MONATOMIC FLUIDS

The free volume equations discussed in Chapters 2-4 accurately predict viscosities and self-diffusion coefficients for nonpolar fluids in the density range  $\rho > 2\rho_c$ . However, the theory cannot be readily extended to include thermal conductivity, and is limited to the above density range. In this chapter and the next a general and direct application of the corresponding states principle is examined. The treatment for monatomic molecules does not assume any simple model, and should be applicable to all transport properties over the entire range of densities and temperatures.

#### 5.1 Molecular Basis of the Correspondence Principle

If correctly applied, the principle of corresponding states provides an accurate and very useful method for predicting physical properties of pure substances, under conditions for which no data are available, from the measured properties of one or more substances. The corresponding states principle has been widely applied to the thermodynamic properties of pure substances; thus the generalized charts of Hougen, Watson and Ragatz (28) and of Hirschfelder, Curtiss and Bird (20) have proven of great practical use in engineering calculations. The principle of corresponding states was first suggested by Van der Waals in 1873 as a result of his equation of state. It was not until 1939, however, that a rigorous and more general theoretical derivation of the principle was attempted by Pitzer (74) for thermodynamic properties using statistical mechanics.

Pitzer presented his derivation based on the following assumptions:

- Assumption 1. Quantum effects are negligible.
- Assumption 2. The intramolecular degrees of freedom (rotational and vibrational) are independent of density.
- Assumption 3. The intermolecular potentials are pairwise additive.
- Assumption 4. The potential energy for a pair of molecules has the form

$$u = \epsilon \phi \left( \frac{r}{\sigma} \right) \quad (5.1)$$

where  $r$  = the intermolecular distance

$\epsilon$  = characteristic energy

$\sigma$  = characteristic distance

$\phi$  = a universal function

Using Assumptions 3 and 4 the configuration energy may be written as

$$U = \sum_{i < j}^N \epsilon \phi \left( \frac{r_{ij}}{\sigma} \right) \quad (5.2)$$

The configurational partition function may then be put in reduced form (50)

$$Z = \frac{1}{N!} \int_0^V \dots \int_0^V \exp \left[ - \frac{\epsilon}{kT} \sum_{i < j}^N \phi \left( \frac{r_{ij}}{\sigma} \right) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N \quad (5.3)$$

$$Z = \frac{\sigma^{3N}}{N!} Z^*(T^*, V^*, N) \quad (5.4)$$

where  $N$  = number of molecules

$$T^* = \frac{kT}{\epsilon} = \text{reduced temperature}$$

$$V^* = \frac{V}{\sigma^3} = \text{reduced molal volume}$$

Since all equilibrium configurational properties of interest may be evaluated from the configurational partition function  $Z$  and its temperature and volume derivatives, equation (5.4) represents a general proof of the principle of corresponding states for thermodynamic properties of pure substances, provided all the above assumptions are observed. Thus the reduced equation of state is

$$\begin{aligned} P^* &= \frac{P\sigma^3}{\epsilon} = \frac{\sigma^3}{\epsilon} kT \left( \frac{\partial \ln Z}{\partial V} \right)_{T,N} \\ &= P^*(T^*, V^*) \end{aligned} \quad (5.5)$$

where it is noted that intensive properties do not depend upon  $N$ .

The principle of corresponding states for thermodynamic properties may also be derived by the method of dimensional analysis (75). However in this method the conditions under which a molecule may obey the corresponding states principle are not explicit.

One way of deriving the principle for transport properties is by dimensional analysis, with the reduction performed using either the critical constants or appropriate combinations of molecular parameters. A rigorous statistical mechanical derivation for transport properties similar to that mentioned above for thermodynamic properties, is possible, as has been shown by Helfand and Rice (76).



The transport coefficients may be expressed in terms of equilibrium time correlation functions. The equations for the shear and bulk viscosity, thermal conductivity and self-diffusion coefficients are given in equations (1.1) to (1.4) of Chapter 1. Using the four assumptions made in deriving the principle for thermodynamic properties, it is possible to put these equations in a reduced form. The derivation of the principle for the self-diffusion coefficient is given below as an example of the procedure.

The self-diffusion coefficient expressed in terms of the time integrals of appropriate autocorrelation function has the form

$$D = \int_0^{\infty} \langle v_x(0) v_x(t) \rangle dt \quad (5.6)$$

Based on Assumptions 1 and 2 given above the time correlation function  $\langle v_x(0) v_x(t) \rangle$  may be written in terms of integrals over phase space

$$\langle v_x(0) v_x(t) \rangle = \frac{\int_{-\infty}^V \dots \int_0^V v_x(0) v_x(t) e^{-\beta H} dp_1 \dots dp_N dr_1 \dots dr_N}{\int_{-\infty}^V \dots \int_0^V e^{-\beta H} dp_1 \dots dp_N dr_1 \dots dr_N} \quad (5.7)$$

Assumption 2 is implicit, since the integrals are performed only over center of mass coordinates. The Hamiltonian  $H$  for the center of mass coordinates is given by

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + U \quad (5.8)$$

and if Assumptions 3 and 4 are satisfied, we may write

$$U = \epsilon \sum_{i < j}^N \phi \left( \frac{r_{ij}}{\sigma} \right) \quad (5.9)$$

Now, if we define reduced quantities as

$$\text{distance} \quad r^* = \frac{r}{\sigma} \quad (5.10)$$

$$\text{temperature} \quad T^* = \frac{kT}{\epsilon} \quad (5.11)$$

$$\text{time} \quad t^* = t \epsilon^{1/2} / m^{1/2} \sigma \quad (5.12)$$

$$\text{momentum} \quad p^* = p / (m^{1/2} \epsilon^{1/2}) \quad (5.13)$$

$$\text{volume} \quad v^* = v / \sigma^3 \quad (5.14)$$

then

$$\begin{aligned} \langle v_x(0) v_x(t) \rangle &= \frac{\frac{\epsilon}{m} \int_{-\infty}^{+\infty} \int_0^{\frac{Nv}{\sigma^3}} p_x^*(0) p_x^*(t^*) \exp \left[ - \sum_{i=1}^N \frac{p_i^{*2}}{2T^*} \right.}{\int_{-\infty}^{+\infty} \dots \int_0^{\frac{Nv}{\sigma^3}} \exp \left[ - \sum_{i=1}^N \frac{p_i^{*2}}{2T^*} \right.} \\ &\quad \left. - \frac{1}{T^*} \sum_{i < j}^N \phi(r_{ij}^*) \right] dp_1^* \dots dp_N^* dr_1^* \dots dr_N^*}{\int_{-\infty}^{+\infty} \dots \int_0^{\frac{Nv}{\sigma^3}} \exp \left[ - \sum_{i=1}^N \frac{p_i^{*2}}{2T^*} \right.} \\ &\quad \left. - \frac{1}{T^*} \sum_{i < j}^N \phi(r_{ij}^*) \right] dp_1^* \dots dp_N^* dr_1^* \dots dr_N^*} = \frac{\epsilon}{m} g(T^*, v^*, t^*) \end{aligned} \quad (5.15)$$

where  $g$  is a universal function of  $T^*$ ,  $v^*$  and  $t^*$ . From equation (5.6)

$$D = \frac{\epsilon^{1/2} \sigma}{m^{1/2}} \int_0^{\infty} g(T^*, v^*, t^*) dt^* \quad (5.16)$$

or combining equations (5.15) and (5.16)

$$D^* = D^*(T^*, V^*) \quad (5.17)$$

where 
$$D^* = \frac{D}{\sigma_q} \sqrt{\frac{m}{\epsilon}} \quad (5.18)$$

Similar relationships may be derived for shear and bulk viscosity and thermal conductivity,

$$\eta^* = \eta^*(T^*, V^*) \quad (5.19)$$

$$\kappa^* = \kappa^*(T^*, V^*) \quad (5.20)$$

$$\lambda^* = \lambda^*(T^*, V^*) \quad (5.21)$$

where 
$$\eta^* = \frac{\eta \sigma^2}{\sqrt{m\epsilon}} \quad (5.22)$$

$$\kappa^* = \frac{\kappa \sigma^2}{\sqrt{m\epsilon}} \quad (5.23)$$

$$\lambda^* = \frac{\lambda \sigma^2}{k} \sqrt{\frac{m}{\epsilon}} \quad (5.24)$$

The corresponding states principle may be derived under less restrictive conditions than those used above. Although it is then of general application it loses the attractive simplicity of the two-parameter laws expressed by equations (5.17), (5.19), (5.20) and (5.21). Thus, Assumption 1 is readily removed by using quantum mechanical expressions in place of integrals over phase space. This results in the introduction of a reduced Planck constant in the expressions for transport properties,

$$D^* = D^*(T^*, V^*, h^*) \quad (5.25)$$

$$\eta^* = \eta^*(T^*, V^*, h^*) \quad (5.26)$$

$$\kappa^* = \kappa^*(T^*, V^*, h^*) \quad (5.27)$$

$$\lambda^* = \lambda^*(T^*, V^*, h^*) \quad (5.28)$$

where

$$h^* = \frac{h}{\sigma \sqrt{m\epsilon}}$$

Donth (77) showed that the corresponding states principle could be proved for thermodynamic properties without assuming pairwise additivity of potentials (Assumption 3). Thus in place of Assumption 3 he assumed that the total potential energy of the system might be expressed in the form

$$U = \epsilon \Phi \left( \frac{r_1}{\sigma}, \frac{r_2}{\sigma}, \dots, \frac{r_i}{\sigma} \right) \quad (5.29)$$

where  $\Phi$  is a universal function of the reduced position coordinates. Recently Hakala (75) derived a more general form of the corresponding states principle for the thermodynamic properties by means of dimensional analysis. The effect of his treatment is to remove Assumption 4. The corresponding states principle is shown to apply to substances which do not obey a pair potential of the form given by equation (5.1), provided the necessary additional reduced parameters are included in the correlation.

It is of interest to note that the above corresponding states relations for  $D$  and  $\eta$  may be derived from the free volume equations.

The assumptions implied are in this case less clearly defined. The expression for self-diffusion coefficient derived from free volume theory is given by equation (2.11) as

$$\frac{D}{T^{1/2}} = B_o \exp \left( - \frac{E_v}{RT} \right) \exp \left( - \frac{V_o}{V - V_o} \right) \quad (5.30)$$

Equation (5.30) can be expressed in terms of reduced variables as

$$\frac{D^*}{T^{*1/2}} = B_o^* \exp \left( - \frac{E_v^*}{T^*} \right) \exp \left( - \frac{V_o^*}{V^* - V_o^*} \right) \quad (5.31)$$

or

$$D^* = D^*(T^*, V^*) \quad (5.32)$$

where

$$E_v^* = \frac{E_v}{N\epsilon} = E_v^*(V^*) \quad (\text{see Chapter 3})$$

$$V^* = \frac{V}{\sigma^3}$$

$$V_o^* = \frac{V_o}{\sigma^3} = V_o^*(T^*) \quad (\text{see Chapter 3})$$

and it is assumed that  $B_o^* = \frac{B_o m^{1/2}}{\sigma k^{1/2}} = \text{constant}$ .

In this chapter we consider only fluids composed of monatomic molecules (excluding He) so that Assumptions 1 and 2 may be regarded as fully satisfied. The inert gas molecules have been found to obey the principle of corresponding states for thermodynamic properties (20,74) and transport properties at low density (78) within experimental accuracy. Pairwise additivity of potentials seems to be a good assumption up to reasonably high densities for the molecules considered in this chapter (79-81). Ross and Alder (82) have presented experimental evidence that nonadditivity becomes a significant

factor for these fluids only at very high densities, of about 4 times the critical value. Assumption 4 concerning the form of the pair potential energy is only approximately satisfied by monatomic molecules considered here, as discussed by Smith (83).

## 5.2 Previous Work

Previous work on the application of the principle to transport coefficients of inert gases and other simple polyatomic molecules in the dense gas and liquid states has been reported by Cini-Castagnoli, Pizzella and Ricci (84), Kerrisk, Rogers and Hammel (85), Rogers and Brickwedde (86), Boon and Thomaes (87,88), Boon, Legros and Thomaes (64), Tee, Kuether, Robinson and Stewart (89), Trappeniers, Botzen, Van Den Berg and Van Oosten (90), and Trappeniers, Botzen, Ten Seldam, Van Den Berg and Van Oosten (91).

Cini-Castagnoli, et al. applied the principle to the viscosity and thermal conductivity of saturated liquid Ar, CO, N<sub>2</sub>, CH<sub>4</sub> and O<sub>2</sub>. Correlations appeared to be poor, especially for the reduced viscosities. Kerrisk et al. and Rogers and Brickwedde examined the principle of corresponding states for the light molecules He<sup>3</sup>, He<sup>4</sup>, H<sub>2</sub>, D<sub>2</sub>, T<sub>2</sub>, etc., where quantum effects are important. They tested the principle for the saturated liquid viscosity and thermal conductivity of these substances. In their correlation they introduced the reduced Planck constant  $h^*$  as a third parameter as required by equations (5.26) and (5.28). Boon et al. tested the validity of the corresponding states principle for the saturated liquid viscosity of Ar, Kr, Xe, O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> and CD<sub>4</sub>. They found that the inert gases obey the principle

closely, but even relatively simple polyatomic molecules such as  $O_2$ ,  $CH_4$  and  $CD_4$  were found to deviate markedly.

Self-diffusion coefficients and binary diffusion coefficients of more than 14 simple molecules in the dilute gas, dense gas and liquid states have been tested by Tee et al. They defined the reduced diffusion coefficient  $D_{AB}^*$  as

$$D_{AB}^* = \frac{c_o D_{AB} \left( \frac{T_{cAB}}{P_{cAB}} \right)}{\sqrt{T_{cAB} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)}} \quad (5.33)$$

where  $c_o$  here represents the total concentration, and obtained from the equation for the diffusion coefficient of a dilute gas the relation

$$D_{AB}^* = 4.05 \times 10^{-6} \frac{\sqrt{\frac{T}{T_{cAB}}}}{\Omega(1,1)^*} \quad (5.34)$$

They plotted their results as  $D_{AB}^*$  against  $P_R$  at constant  $T_R$  where  $P_R = \frac{P}{P_c}$  and  $T_R = \frac{T}{T_c}$ . However, the data they present seem to be too scattered to justify the test.

Trappeniers et al. applied the corresponding states principle to the viscosity of inert gases up to high densities for temperatures above critical. They defined the reduced viscosity as

$$Q^* = \frac{\eta^*}{\eta_o^*} \quad (5.35)$$

where

$$\eta_o^* = \frac{5}{16 \pi} \frac{T^*}{\Omega(2,2)^*} \quad (5.36)$$

and

$$\eta^* = \frac{\eta \sigma^2}{\sqrt{m \epsilon}} \quad (5.37)$$



$Q^*$  was then related to  $\rho^*$  and  $T^*$ .

### 5.3 Test of Correspondence Principle for Inert Gases

No systematic and consistent test of the principle for all three transport properties of dense fluids over a wide range of temperatures and densities seems to have been made. In particular the transport properties of fluids at very high pressures (and thus high densities) have not been examined. The behavior at high densities is of particular interest since it is under these conditions that Assumption 3 may become invalid. Also, errors arising from differences in the repulsive portion of the intermolecular potential for the molecules considered (Assumption 4) may become apparent at high density.

The essential simplifying factor in the case of monatomic (as opposed to polyatomic) molecules is that Assumption 2 is fully satisfied. A comparison of the correspondence behavior for monatomic and polyatomic molecules may therefore throw light on the validity of this assumption. Calculations are presented in this chapter to test the correspondence principle for all three transport coefficients over the full range of temperatures and pressures for which data are available. The extension to polyatomic molecules is discussed in the following chapter.

Reduction of the transport coefficients are performed using Lennard-Jones [6,12] potential parameters rather than critical constants because the former have more theoretical significance. The use of critical constants is justified when the group of substances accurately obey the same potential function, Assumption 4 (50). In such a case it would in principle be immaterial whether potential function or



critical parameters were used. However, in practice the group of molecules do not all accurately obey Assumption 4, and the potential parameters are force-fitted to some semi-empirical equation, in this case the Lennard-Jones [6,12] potential function. Under such conditions the use of potential parameters rather than critical constants may improve the correlation obtained. In this work, reduction with both critical constants and potential parameters (smoothed in the way described below) was tried. The use of potential parameters was found to give consistently better results.

The potential parameters reported in the literature by different workers show substantial variations. Thus for krypton values of  $\epsilon$ , the characteristic energy, reported by different authors vary by as much as 14%. It is therefore desirable to find some means of averaging these parameters. Moreover, Reed and McKinley (92) have shown that polyatomic molecules do not all obey the simple two-parameter Lennard-Jones [6,12] potential energy function. Since Assumption 4 requires that all molecules should obey the same potential energy function in order to arrive at the same corresponding states, an attempt was made to force the polyatomic molecules to fit a two-parameter potential energy function by adopting the method used by Tee, Gotoh and Stewart (93). According to the Pitzer compressibility correlation (94) the volumetric behavior of a fluid, and thus the intermolecular forces present, are characterized by  $P_c$ ,  $T_c$  and the acentric factor  $\omega$ . Thus the intermolecular force constants  $\epsilon$  and  $\sigma$  should depend on these three quantities, so that one obtains the

dimensionless relations

$$\frac{\epsilon}{kT_c} = f(\omega) \quad (5.38)$$

$$\left( \frac{P_c}{kT_c} \right)^{1/3} \sigma = f'(\omega) \quad (5.39)$$

where  $f$  and  $f'$  are universal functions. In Figures 5.1 and 5.2 values of  $\left( \frac{P_c}{kT_c} \right)^{1/3} \sigma$  and  $\frac{\epsilon}{kT_c}$  for twenty different molecules are plotted against their corresponding Pitzer factor  $\omega$ . The best straight lines were drawn through them by the method of least squares. Potential parameters used in these figures were values calculated from gas viscosity data, and were taken from Hirschfelder, Curtiss and Bird (20) and Tee, Gotoh and Stewart (93). Where several values for  $\epsilon$  and  $\sigma$  were reported for a given molecule the mean values are plotted in Figures 5.1 and 5.2, and the maximum deviation is indicated. The calculations presented in this chapter and the next make use of smoothed potential parameters obtained from these two figures. Values of the potential parameters used are shown in Tables 5.1 and 6.1. Values for molecules other than those tabulated may be calculated from the equations for the best lines shown in Figures 5.1 and 5.2 which are

$$\frac{\epsilon}{kT_c} = 0.7932 - 0.6723\omega \quad (5.40)$$

$$\left( \frac{P_c}{kT_c} \right)^{1/3} \sigma = 0.4583 + 0.1213\omega \quad (5.41)$$

Figures 5.3, 5.4 and 5.5 are reduced plots of saturated liquid viscosity, thermal conductivity and self-diffusion coefficient as

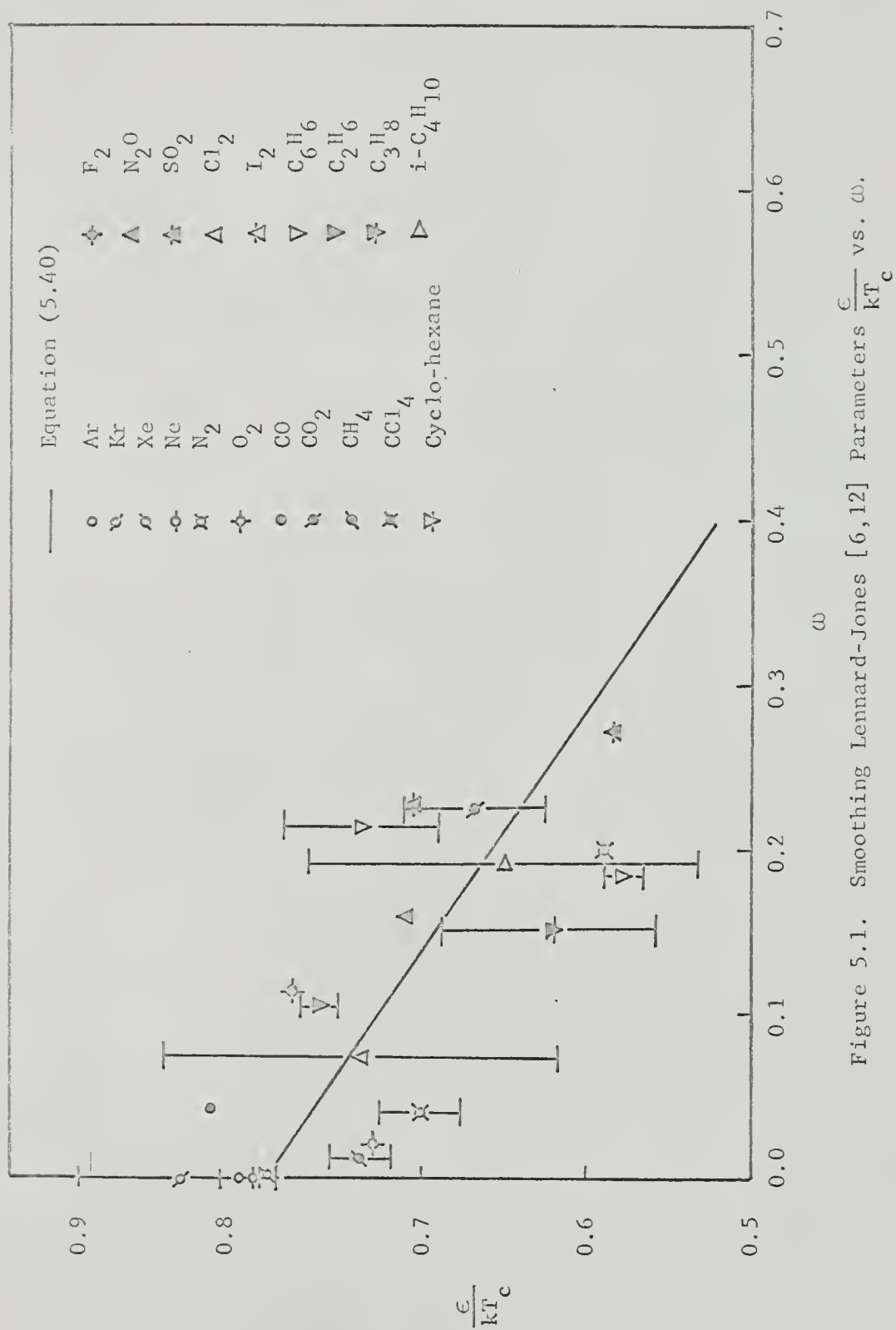


Figure 5.1. Smoothing Lennard-Jones [6,12] Parameters  $\frac{\epsilon}{kT_c}$  vs.  $\omega$ .

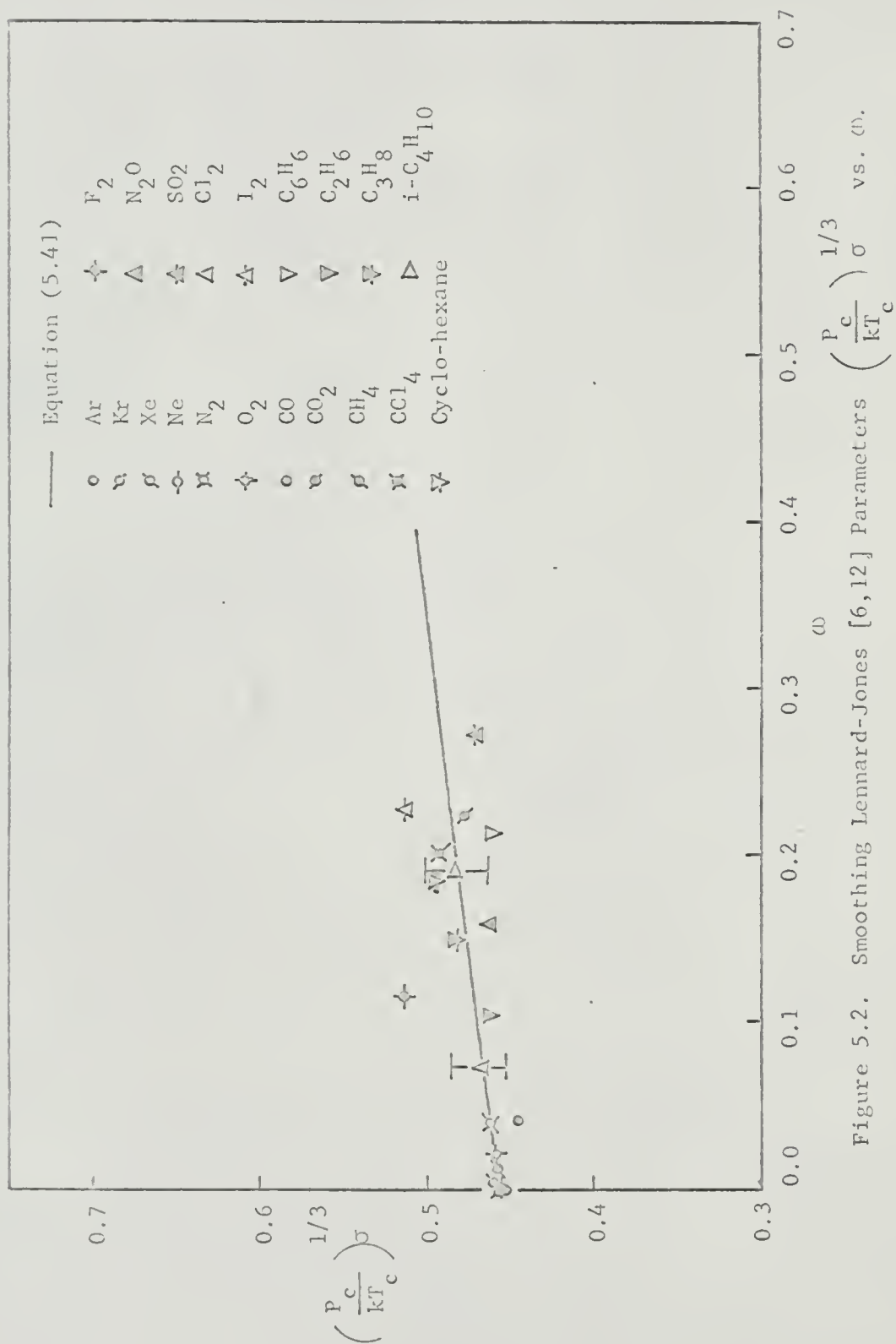


Figure 5.2. Smoothing Lennard-Jones [6,12] Parameters  $\left(\frac{P_c}{kT_c}\right)^{1/3} \sigma$  vs.  $\left(\frac{P_c}{kT_c}\right)^{1/3} \sigma$ .

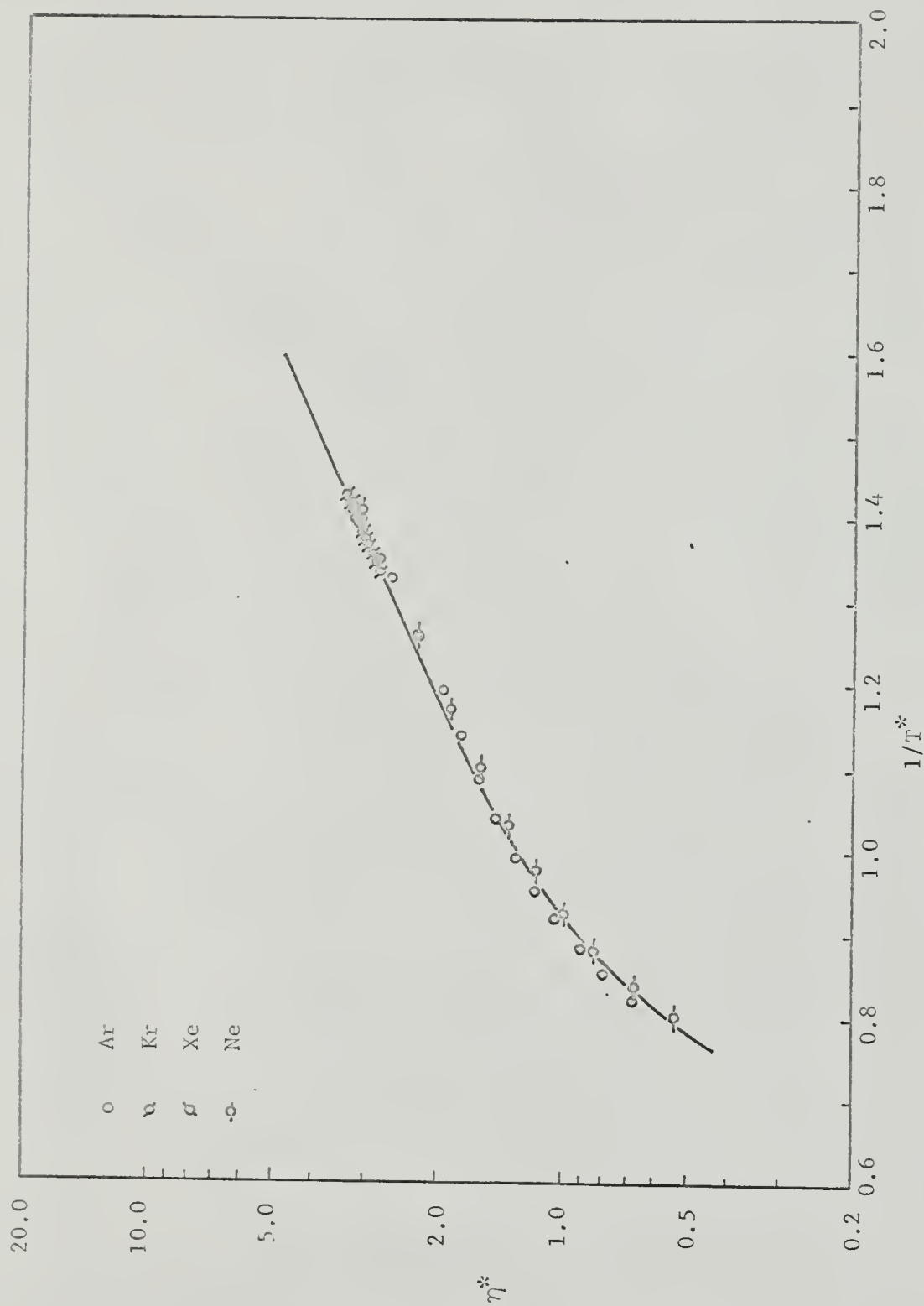


Figure 5.3. Correspondence Principle for Saturated Liquid Viscosity - Monatomic Molecules.

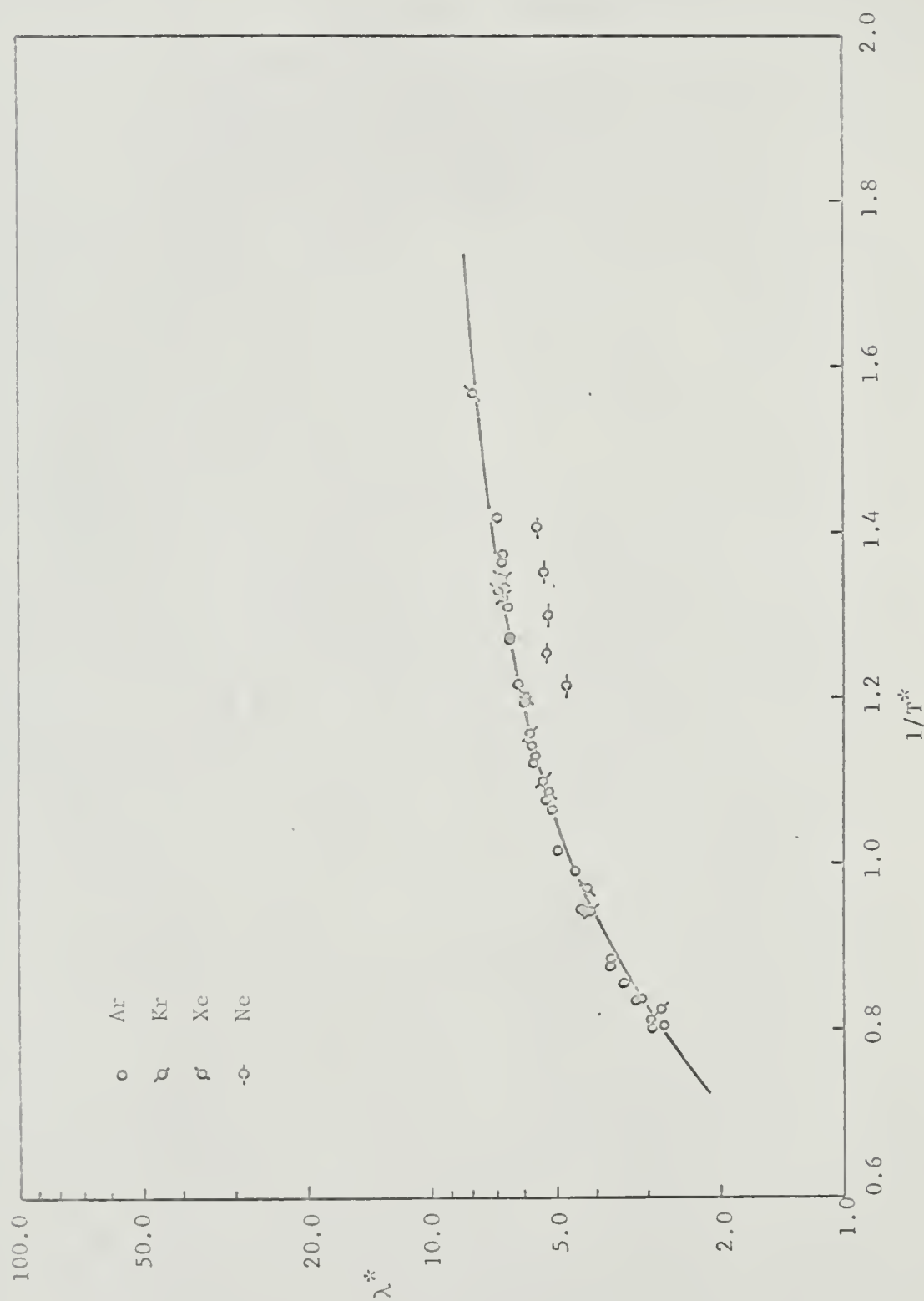


Figure 5.4. Correspondence Principle for Saturated Liquid Thermal Conductivity - Monatomic Molecules

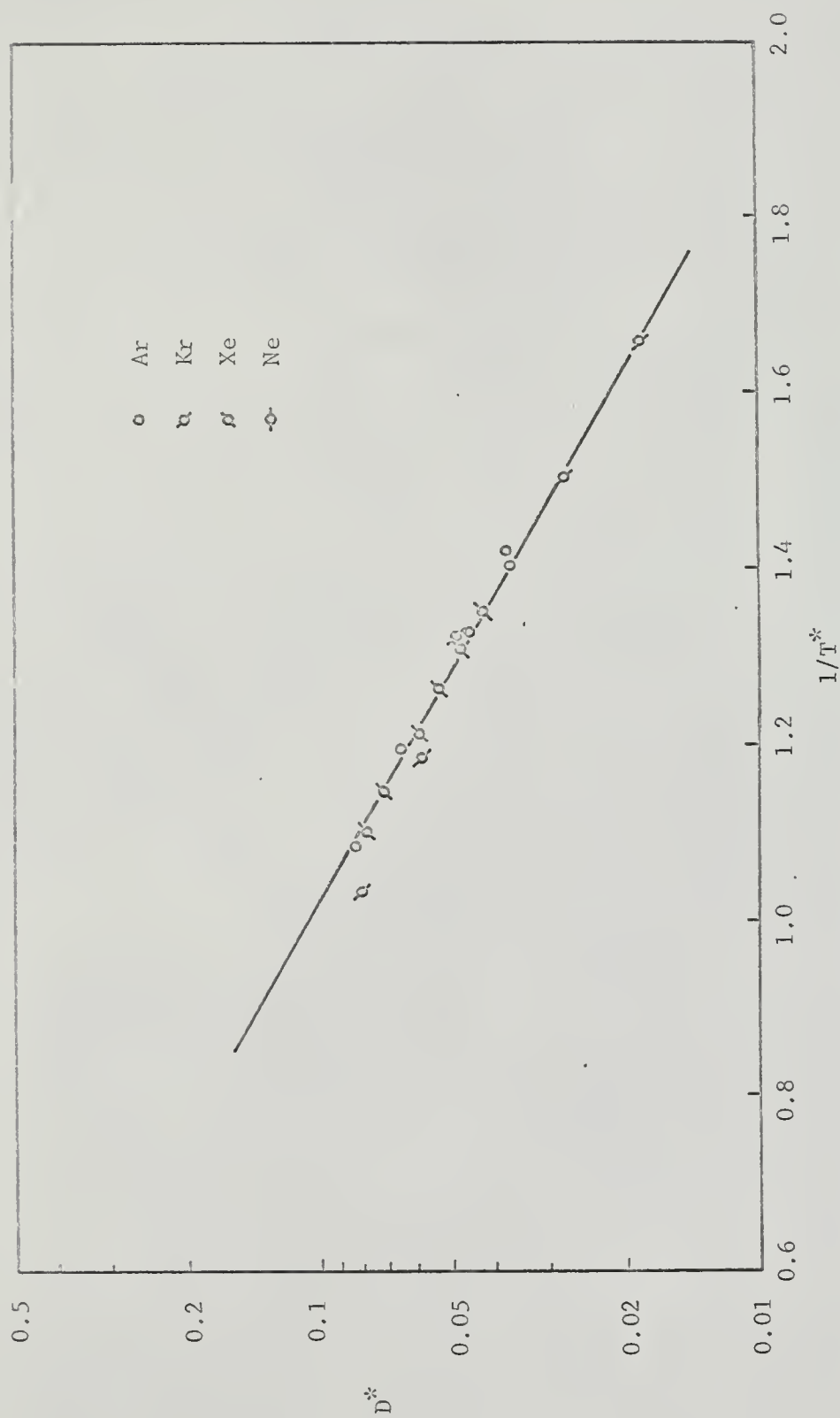


Figure 5.5. Correspondence Principle for Saturated Liquid Self-Diffusivity - Monatomic Molecules.

functions of temperature for the inert gases (argon, krypton, xenon and neon). For pure saturated liquids there is only one degree of freedom, and the reduced transport coefficients depend only on reduced temperature. In the saturated liquid region, the inert gases appear to obey the corresponding states principle for the above transport properties reasonably well with the exception of the thermal conductivity data of neon. The discrepancy observed in Figure 5.4 for neon may be due to quantum effects, since neon is the second lightest molecule among the inert gases. Experimental data for bulk viscosity are scarce. The only bulk viscosity measurements made seem to be those reported by a few workers for argon (14,95,96). Figure 5.6 is a reduced plot of bulk viscosity of saturated liquid argon (extrapolated data) as a function of temperature. Great experimental difficulties are involved in bulk viscosity measurements, and the data are very scattered. Even among the data of the same worker the average percent deviation is as much as 15%.

In the derivation of the correspondence principle for transport properties shown above, reduced viscosity is found to be a function of reduced temperature and reduced molal volume. Thus according to equation (5.19)  $\eta^* = \eta^*(T^*, V^*)$ . However it is more convenient in practice to plot the transport properties as a function of temperature and pressure. Since reduced molal volume may be shown to be related to reduced pressure through the equation of state, one may express  $\eta^*$  as  $\eta^*(T^*, P^*)$ .

Reduced viscosities of inert gases plotted as a function of reduced temperature at constant reduced pressures are shown in



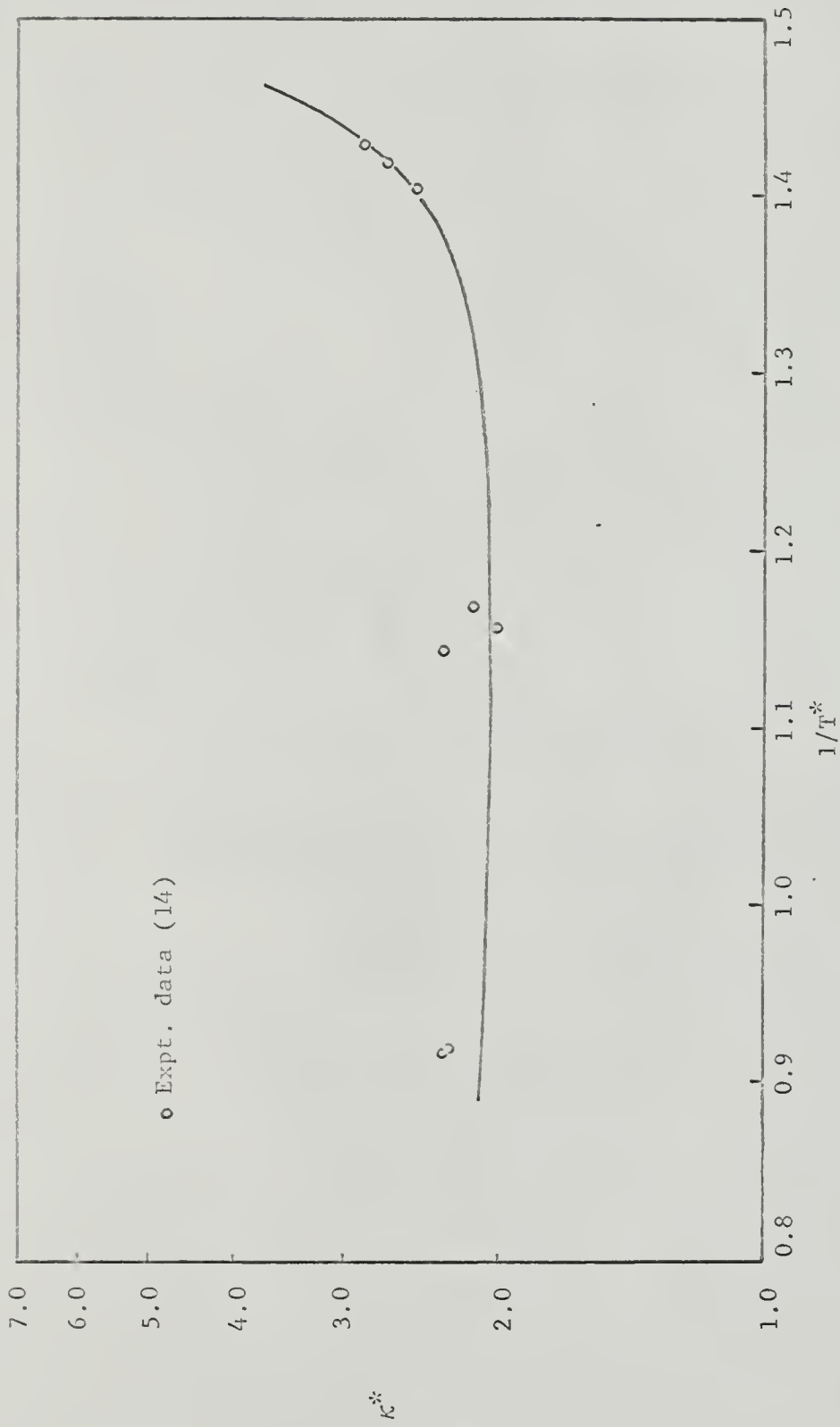


Figure 5.6. Reduced Bulk Viscosity of Saturated Liquid Argon.

Figure 5.7. The corresponding states principle appears to apply closely to viscosity of inert gases over the entire range of temperature and pressure for which experimental data are available. Data plotted in Figure 5.7 cover densities from the dilute gas phase to the dense gas and liquid phase, and correspond to pressures from zero to over 2000 atmospheres. A similar plot for the thermal conductivity of inert gases is shown in Figure 5.8. In this plot the correspondence principle is found to apply well for argon, krypton and xenon over the entire temperature and pressure range for which data are available. The neon data in Figure 5.8 obey the simple correspondence principle at high temperatures, but not at low temperatures. This behavior for neon suggests that quantum effects are important for this fluid at low temperatures.

The reduced viscosity and reduced thermal conductivity data are found to fit equations of the form

$$\ln \eta^* = a_1 + a_2 T^{*-1} + a_3 T^{*-2} + a_4 T^{*-3} + a_5 T^{*-4} \quad (5.42)$$

and

$$\ln \lambda^* = b_1 + b_2 T^{*-1} + b_3 T^{*-2} + b_4 T^{*-3} + b_5 T^{*-4} \quad (5.43)$$

at constant reduced pressure or along the saturation curve. The reduced self-diffusion coefficient, on the other hand, is found to fit an equation of the form

$$\ln D^* = d_1 + d_2 T^{*-1} \quad (5.44)$$

The principal parameters used to test the correspondence principle for monatomic molecules are shown in Table 5.1. The

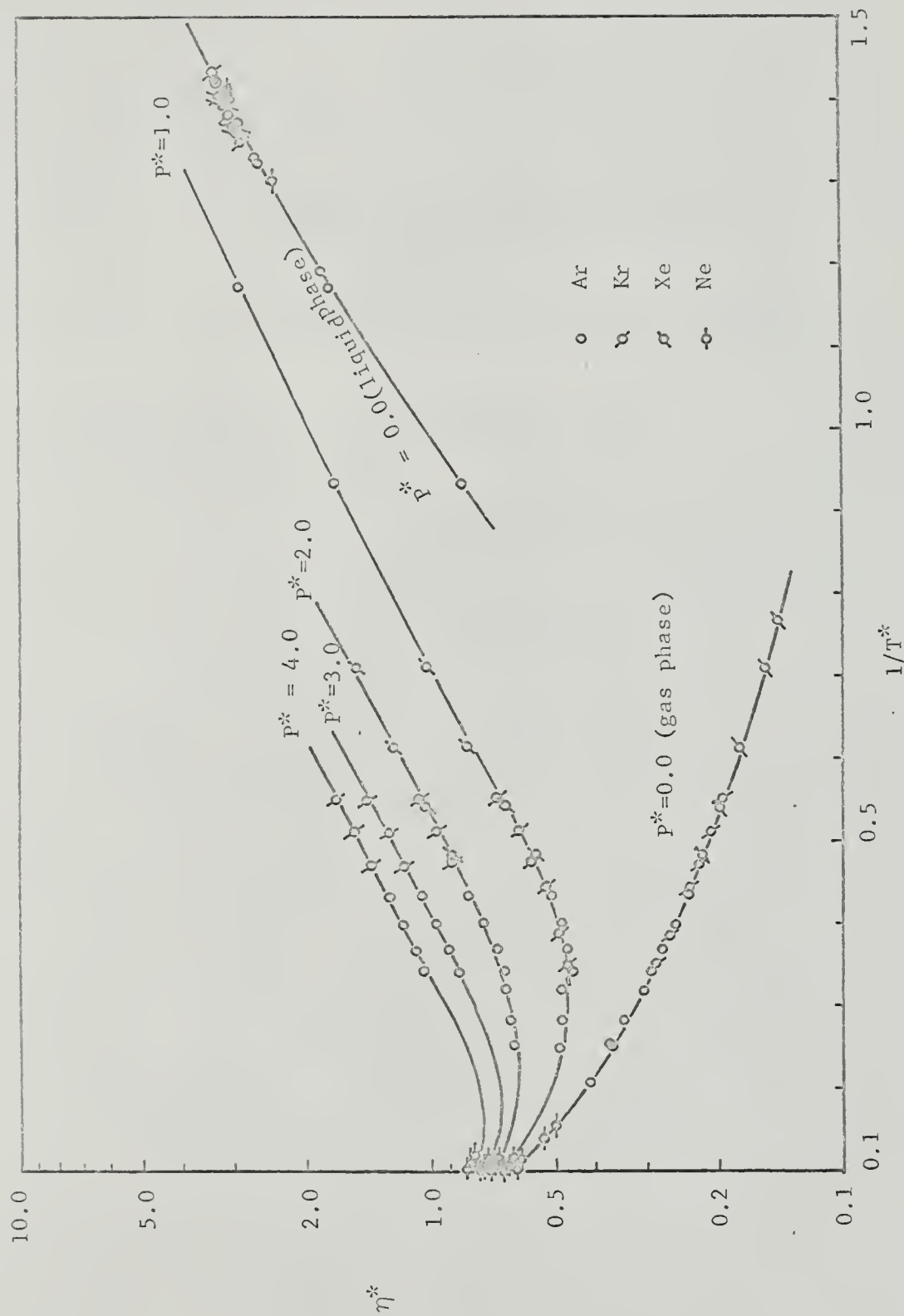


Figure 5.7. Reduced Viscosity Isobars as Functions of Reduced Temperature - Monatomic Molecules.

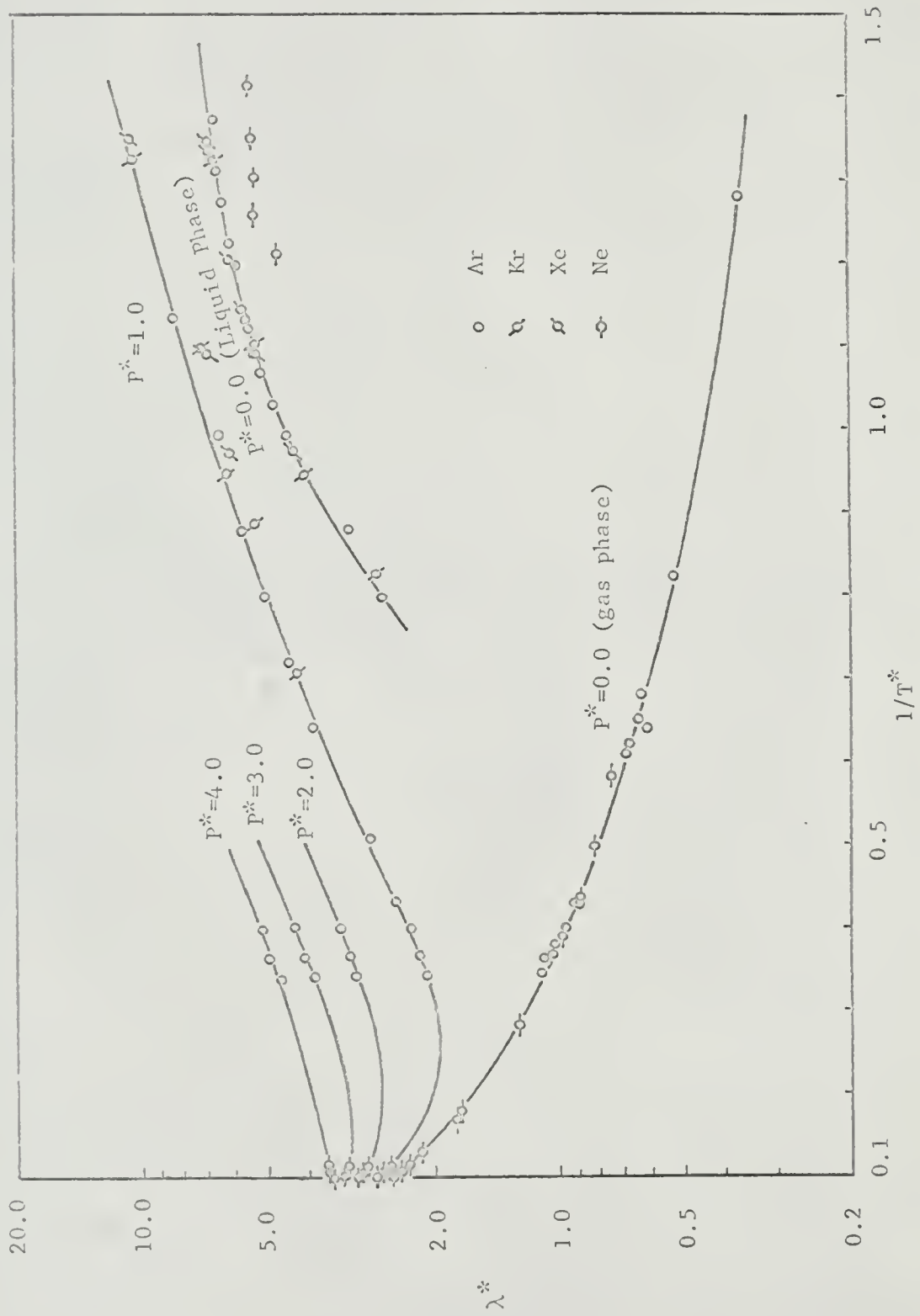


Figure 5.8. Reduced Thermal Conductivity Isobars as Functions of Reduced Temperature - Monatomic Molecules.

TABLE 5.1

PARAMETERS FOR MONATOMIC MOLECULES

Molecule	Smoothed Pot. Parameters				
	$\sigma(\text{\AA})$	$\epsilon/k$ ( $^{\circ}\text{K}$ )	$T_c$ ( $^{\circ}\text{K}$ )	$P_c$ (atm.)	$M$
Ne	2.79	35.30	44.50	26.90	20.18
Ar	3.45	119.77	151.00	48.00	39.95
Kr	3.70	166.10	209.40	54.30	83.80
Xe	4.03	229.83	289.75	58.00	131.30
					$\omega$
					0.00
					0.00
					0.00
					0.00

potential parameters included in this table are obtained from Figures 5.1 and 5.2. The coefficients of equation (5.42) evaluated by computer for saturated liquid viscosity of monatomic molecules (Ar, Kr, Xe, Ne) together with the average error between the equation and experiment are shown in Table 5.2. The average percentage errors between prediction and experiment for the inert gases are within 4%, and this is of about the same order as the experimental accuracy. Tables 5.3 and 5.4 exhibit the coefficients of equations (5.43) and (5.44) respectively for monatomic fluids. The maximum disagreement between reported thermal conductivity data of different workers for monatomic molecules is estimated to be approximately 7%. Equation (5.43) when used with the values of coefficients shown in Table 5.3 gives an average percentage error well within 4% (thermal conductivity data of neon were not used to fit the coefficients). Disagreements between self-diffusion coefficient data of different workers are especially large. Thus the self-diffusivity of xenon reported by two workers differ by as much as 100% (18,57). Equation (5.44) for self-diffusivity of monatomic molecules using the values of coefficients in Table 5.4 yields an average percentage error of about 5%. Only the data of Naghizadeh and Rice (18) were used in obtaining these coefficients.

Table 5.5 lists the coefficients of the viscosity equation together with percentage errors for the viscosity isobars shown in Figure 5.7. The average errors are largest at the highest reduced pressures, which correspond to pressures up to approximately 2000 atmospheres. These larger errors may be due to a failure of

TABLE 5.2

COEFFICIENTS OF SATURATED LIQUID VISCOSITY EQUATION  
FOR MONATOMIC MOLECULES

Molecule	Viscosity Reference	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	Number of Points	Average % Error Y
Ar	97,48,67, 98,61,99, 60	-2.5530	-9.4789	32.0680	-27.5130	7.7083	13	3.4
Kr	64						9	3.2
Xe	64,65						6	2.3
Ne	61,62						11	4.0

$$1 \quad Y = \left\{ \frac{\sum_{i=1}^N \left[ \frac{\eta(\text{expt})_i - \eta(\text{predict})_i}{\eta(\text{predict})_i} \right]^2}{N} \right\}^{1/2} \times 100$$

Overall Y = 3.4%

<sup>2</sup> Overall Y = Average % error of equation from experiment with respect to all the molecules listed.

TABLE 5.3

COEFFICIENTS OF SATURATED LIQUID THERMAL CONDUCTIVITY  
EQUATION FOR MONATOMIC MOLECULES

Molecule	Thermal Conductivity Reference	$b_1$	$b_2$	$b_3$	$b_4$	$b_5$	Number of Points	Average % Error Y
Ar	27, 60, 17, 100, 101, 102, 66						24	3.8
Kr	100, 60, 17	-2.3001	2.7846	5.9641	-6.9168	1.9842	6	3.5
Xe	100, 60, 17						7	2.1
Ne	103						-	-

Overall Y = 3.5



TABLE 5.4

COEFFICIENTS OF SATURATED LIQUID SELF-DIFFUSIVITY EQUATION  
FOR MONATOMIC MOLECULES

Molecule	Self-Diffusion Coefficient Reference	$d_1$	$d_2$	Number of Points	Average % Error Y
Ar	18			5	4.9
Kr	18	0.1753	-2.4798	5	7.4
Xe	18			6	2.3

Overall Y = 5.2%

TABLE 5.5

COEFFICIENTS OF HIGH PRESSURE VISCOSITY EQUATIONS  
FOR MONATOMIC MOLECULES

Molecule	Reduced Pressure $P^*$	Reduced Temp. Range	Viscosity Reference	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	Num-ber of Pts.	Average %Error Y
Ar, Kr Xe, Ne	0.0 (Gas Phase)	1.4-10	104,105,65 33,106,90 107	0.3555	-9.4043	22.2370	-29.3070	14.6300	29	1.0
Ar, Kr Xe, Ne	0.0 (Liquid)	0.7-1.1	15,48,108 64,61,62	-1.5630	0.3337	0.0345	2.2716	-1.0578	23	2.0
Ar, Kr Xe, Ne	1.0	0.8-10	105,65,48 48,33,90	0.3058	-8.4872	20.8840	-16.8700	4.8566	22	2.3
Ar, Kr Xe, Ne	2.0	1.4-10	105,65,48 33,65,90	0.0016	-4.1778	9.6839	-1.0064	-4.5230	17	1.1
Ar, Kr Ne	3.0	1.8-10	105,33,90	-3.4457	51.6950	-260.68	529.70	-371.00	10	6.4
Ar, Kr Ne	4.0	1.8-10	105,33,90	-3.4579	52.2910	-259.08	523.04	-365.58	10	6.4

Assumption 3 at these high pressures, or to experimental errors. The coefficients of the thermal conductivity equations for the isobars shown in Figure 5.8 and the average percentage error between experiment and the equations are given in Table 5.6. The errors for all the equations are within experimental error. Sources of viscosity, thermal conductivity and self-diffusion coefficient data are also included in Tables 5.2 - 5.6.

#### 5.4 Summary

The good agreement of the experimental data with the principle of corresponding states leads one to conclude that the 4 assumptions on which the molecular derivation is based are good approximations for monatomic fluids. An exception is neon, for which quantum effects must be taken into account at low temperatures. It is of particular interest that Assumption 3 concerning pairwise additivity of the intermolecular potential does not lead to significant errors even at the highest densities for which measurements are available. Similarly, Assumption 4 does not give rise to significant errors for these fluids in spite of known differences in the potential energy form (83).

TABLE 5.6

COEFFICIENTS OF HIGH PRESSURE THERMAL CONDUCTIVITY  
EQUATIONS FOR MONATOMIC MOLECULES

Molecule	Reduced Pressure $P^*$	Reduced Temp. Range	Thermal Conductivity Reference	$b_1$	$b_2$	$b_3$	$b_4$	$b_5$	Num- ber of Points	Average % Error Y
Ar, Ne	0.0 (Gas Phase)	0.8-10.0	17, 109, 101, 102, 66	1.4883	-6.9592	11.310	-10.056	3.3428	27	3.6
Ar, Kr, Xe	0.0 (Liquid Phase)	0.7-1.2	17, 101, 100, 110, 60, 103, 111	-3.8454	6.7010	2.3399	-5.4856	1.7863	24	1.8
Ar, Kr, Xe, Ne	1.0	0.7-10	17, 109, 111	1.6577	-8.4336	23.236	-21.202	6.5970	23	1.6
Ar, Ne	2.0	2.5-10	109, 111	2.4580	-26.681	177.06	-485.65	475.60	6	0.8
Ar, Ne	3.0	2.5-10	109, 111	2.4122	-25.395	178.10	-496.82	488.52	6	0.9
Ar, Ne	4.0	2.5-10	109, 111	1.9071	-18.188	162.55	-516.51	547.93	6	1.5

## CHAPTER 6

### PRINCIPLE OF CORRESPONDING STATES FOR POLYATOMIC NONPOLAR FLUIDS

It has long been realized that the simple correspondence principle does not apply accurately to polyatomic fluids in the condensed phase. In the previous chapter it has been shown that monatomic molecules obey the principle of corresponding states over the entire range of temperature and pressure conditions. In this chapter a careful re-examination of the four basic assumptions used in deriving the principle is first made. A simple model of the molecular behavior of a polyatomic liquid is proposed, and provides the basis for a rederivation of the correspondence principle.

#### 6.1 Problems in Polyatomic Fluids

Polyatomic fluids should obey Assumption 1 closely since their molecular weights are usually large and thus quantum effects are negligible. Assumption 3 concerning pairwise additivity of potentials does not seem to be a major source of error for either monatomic or polyatomic fluids (81). Therefore it appears likely that the deviation of polyatomic fluids from the correspondence principle is due to the fact that they do not satisfy either or both Assumptions 2 and 4.

Two-parameter potential energy functions, such as the Lennard-Jones [6,12] equation, do not accurately account for properties of polyatomic fluids (92). In fact three-parameter energy functions, such as the Lennard-Jones [6,n] or the Kihara potential give better results for these molecules. Thus polyatomic fluids in general do not satisfy Assumption 4 closely. Failure of polyatomic fluids to satisfy

Assumption 4 may be corrected by introducing a suitable third parameter. Alternatively a two-parameter potential may be used, taking suitable potential parameters in the way suggested by Tee, Gotoh and Stewart (93).

Recently Preston, Chapman and Prausnitz (112) examined the corresponding states principle for the transport coefficients of nine monatomic and polyatomic fluids in the saturated liquid state. They proposed that potential parameters of substances in the liquid state may take different values from those in the gaseous state. Liquid phase potential parameters were obtained from the saturated liquid viscosity and thermal conductivity data by assuming that the simple correspondence principle applied. They then used these parameters to test the correspondence principle for the saturated liquid viscosity, thermal conductivity and self-diffusion coefficient of the nine molecules. This procedure gave reasonably good correlations for liquid viscosity and thermal conductivity, with root-mean-square deviations of 7.4% and 5.4% respectively. The correlation for self-diffusion coefficient was comparatively poorer, showing a root-mean-square deviation of 15%. Their treatment seems open to criticism on several counts. Firstly, by force-fitting the parameters using liquid phase data the validity of their test is doubtful. In particular, certain facets of the behavior of polyatomic molecules may be hidden in this way; thus hindered rotation in the liquid state may be important, as discussed below. Further, because separate sets of potential parameters are necessary for the gas and liquid phases, problems will arise in choosing the most suitable parameters for the intermediate densities,

and it will not be possible to predict transport properties when no experimental liquid phase data are available.

Little attention seems to have been given previously to the possible failure for liquids of Assumption 2 concerning the density independence of intramolecular degrees of freedom. Because vibrational quanta and bond energies are large one would not expect intermolecular forces to have much effect on the vibrational energy of a polyatomic molecule. However, rotational energies are smaller and it seems quite likely that free rotation of polyatomic molecules may not be possible at high densities.

Figure 6.1 shows a plot of  $\eta^*$  at  $P^* = 0$  for a variety of monatomic and polyatomic molecules in both the gas and liquid states. Reduction of the dilute gas and liquid viscosity coefficients is performed using smoothed molecular parameters determined from gas viscosity data (see Figures 5.1 and 5.2). In the dilute gas phase both monatomic and polyatomic molecules obey the correspondence principle very well. In the liquid phase, however, only the monatomic molecules obey the principle. Deviations for the polyatomic molecules increase as the density increases. Were these deviations due only to incorrect potential parameters, as suggested by Preston et al. (112), one would expect that discrepancies might occur for monatomic molecules in the liquid state also. The fact that gas-phase parameters work well for the latter molecules in the liquid states, together with the excellent agreement found for polyatomic fluids at low density, strongly suggests a failure of Assumption 2 in the liquid phase. It

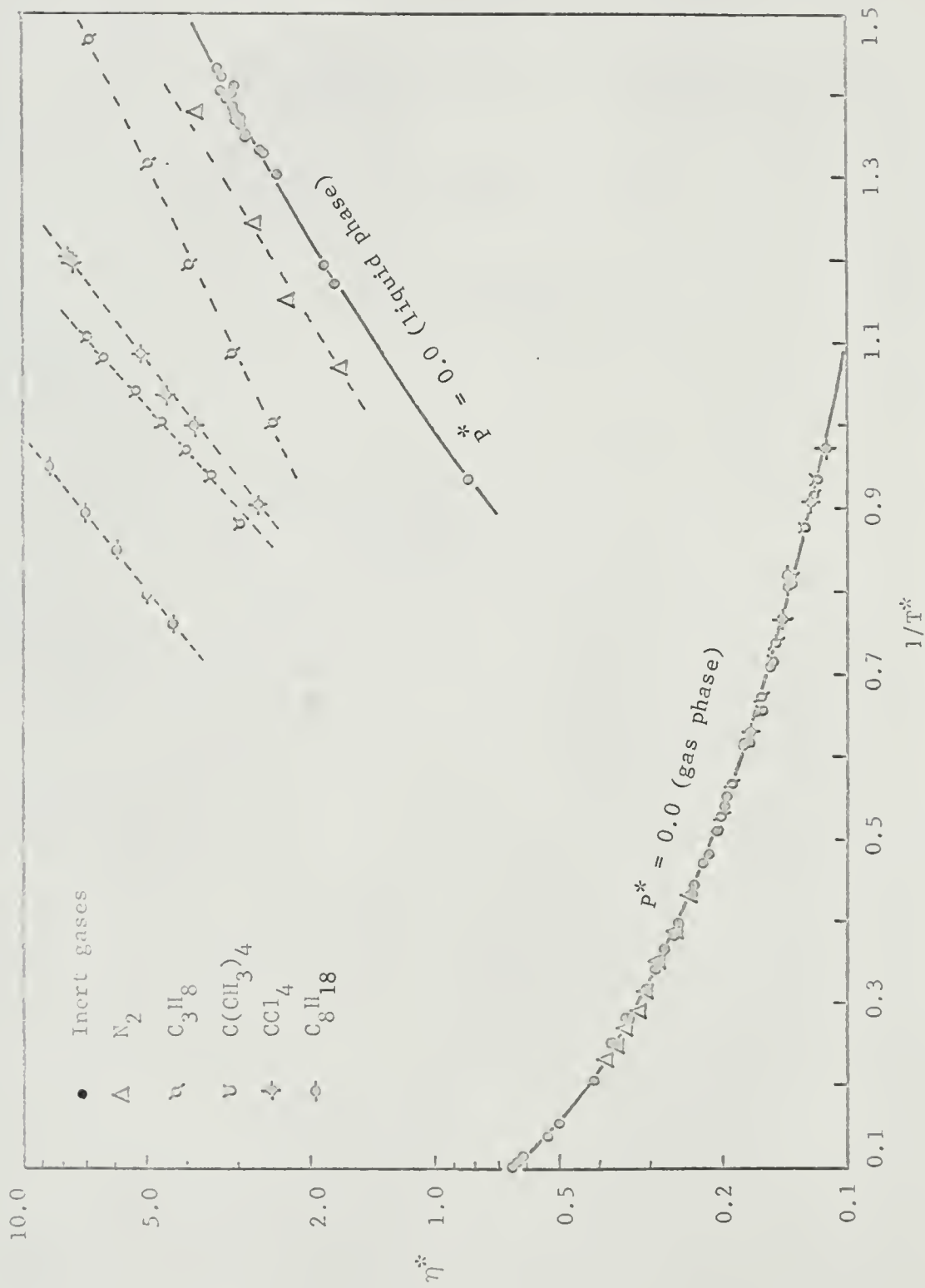


Figure 6.1. Simple Correspondence Principle - Polyatomic Molecules.



seems likely, therefore, that hindered rotation has a significant effect on the transport coefficients of polyatomic fluids at high densities, and that this effect causes increasingly large deviations as density rises. Davis and Matheson (113) have presented evidence to show that rotational degrees of freedom are restricted at high densities.

Figure 6.2 shows reduced viscosity for 20 saturated liquids. The same trends as in Figure 6.1 are seen; deviations from the curve for monatomic liquids are greatest for molecules having larger Pitzer factors.

## 6.2 Derivation of Corresponding States Principle for Polyatomic Molecules

In the gas phase molecular separations are usually large and intermolecular forces are small. A molecule can therefore rotate freely about its body axes. However, as the density increases intermolecular forces become more important, and if these forces are non-central the molecules exert a torque on one another. Polyatomic molecules thus rotate in a potential energy field which is a function of the relative orientations and center of mass positions of the molecules; in the case of very high densities the rotational motion might be reduced to that of angular vibrations about the body axes.

For dense fluids the rotational degrees of freedom thus become dependent on the center of mass coordinates, and cannot be factored out from the phase integral as in the case of dilute gases. The time correlation function instead should be written as

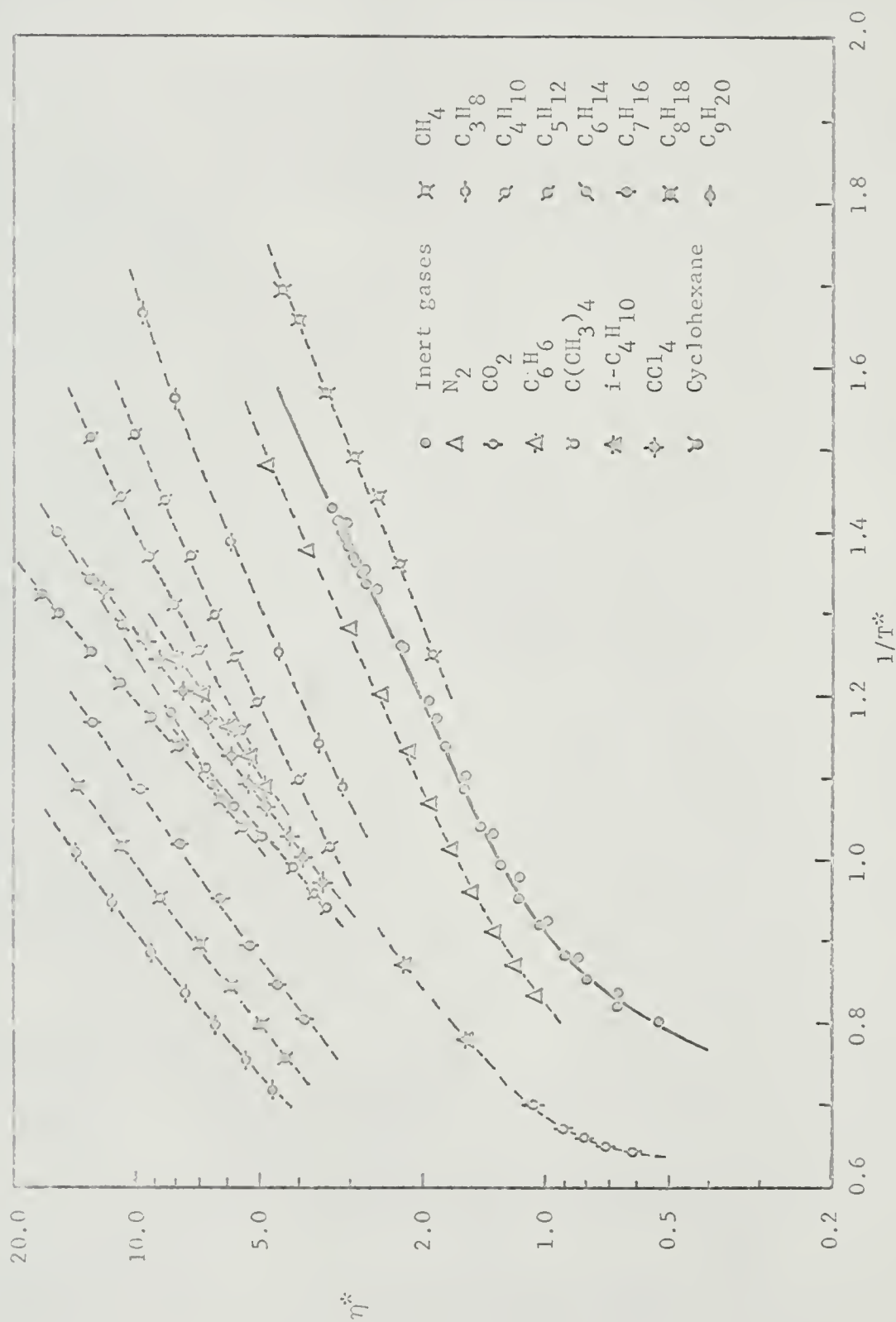


Figure 6.2. Simple Correspondence Principle for Saturated Liquid Viscosity - Polyatomic Molecules.

$$\langle V_x(0)V_x(t) \rangle = \frac{\int \dots \int V_x(0)V_x(t) e^{-H/kT} d\underline{p}_{r_1} \dots d\underline{r}_N d\underline{p}_{\theta_1} \dots d\underline{\theta}_N}{\int \dots \int e^{-H/kT} d\underline{p}_{r_1} \dots d\underline{r}_N d\underline{p}_{\theta_1} \dots d\underline{\theta}_N} \quad (6.1)$$

$$\text{where } H(\underline{p}_{r_1} \dots \underline{r}_N \dots \underline{p}_{\theta_1} \dots \underline{\theta}_N) = K_{CM}(\underline{p}_{r_1} \dots) + K_{rot}(\underline{p}_{\theta_1} \dots) \\ + U(\underline{r}_1 \dots \underline{\theta}_1 \dots)$$

The phase integral in this form will be difficult to handle, since we have little knowledge as to the form of the potential energy term. Although the kinetic energies of translation ( $K_{CM}$ ) and rotation ( $K_{rot}$ ) are separable, the potential energy term is not. Evaluation of the integrals therefore requires that a suitable expression be obtained for  $U(\underline{r}, \underline{\theta})$ . The part of the Hamiltonian arising from intramolecular vibrations is here assumed to be separable and independent of density for the reasons discussed above.

To account in an approximate way for the coupling between translational and rotational degrees of freedom, a highly simplified one-dimensional model is proposed. Consider a harmonic oscillator cell model similar to the type used by Prigogine (50). In this model each molecule is assumed to spend a large fraction of its time oscillating in a cell or cage. Since the oscillator is assumed harmonic, the restoring force acting on a molecule at any time is proportional to the displacement of the molecule from its equilibrium position along each of its orthogonal coordinates. The nearest neighbor molecules are assumed in an average situation to be on their lattice sites, and

are treated as smeared over a sphere passing through their lattice positions. For the present a one-dimensional motion is assumed. However, it can be readily extended to the three-dimensional case by assuming an isotropic system in which the motion along any of the 3 axes is the same.

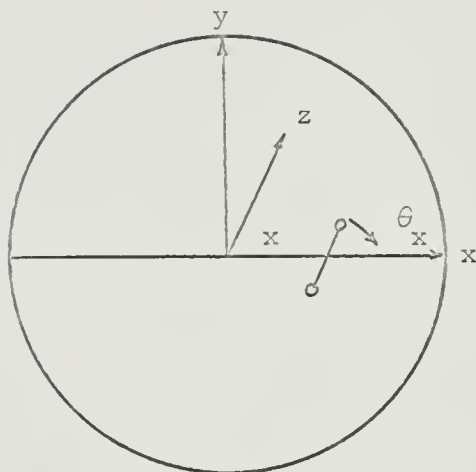


Figure 6.3. A One-Dimensional Oscillator Model.

Consider a molecule oscillating linearly along the x-axis in a cell (Figure 6.3). For convenience the molecule is represented as a rigid diatomic one, but similar considerations will apply in general. Because of the linear oscillation, the molecule rotates in an oscillating potential field, and this gives rise to hindered rotation. The rotational motion of the molecule about the z-axis (perpendicular to the plane of the paper) may be considered to consist of two parts: a constant velocity rotation plus a harmonic angular oscillation superimposed on it. The harmonic angular oscillation is assumed to be

in phase with the linear oscillator. The constant velocity rotation is the value that would be observed if no linear oscillation occurred, that is when the molecule remained at 0. The angular coordinates can be written as

$$\theta_x(x,t) = \Phi_x(t) + \Psi_x(x) \quad (6.2)$$

$$p_{\theta_x}(x) = p_{\Phi_x} + p_{\Psi_x}(x) \quad (6.3)$$

where  $\Phi_x(t)$  and  $p_{\Phi_x}$  refer to the constant velocity rotational motion at 0, while  $\Psi_x(x)$  and  $p_{\Psi_x}(x)$  account for the superimposed oscillation or angular perturbation.

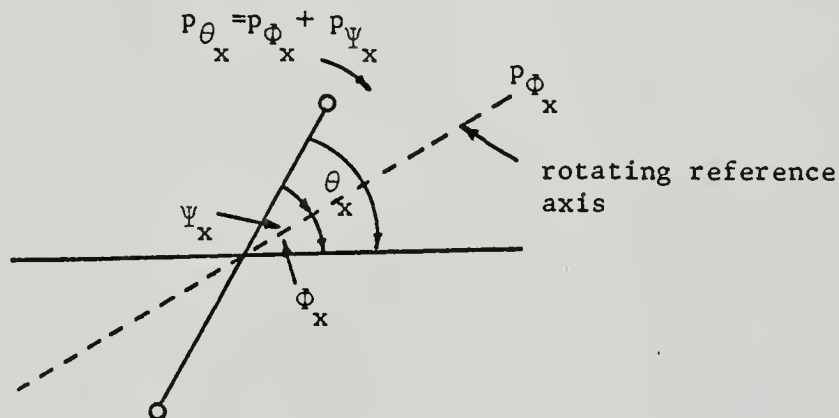


Figure 6.4. Superimposed Rotational Motions of a Molecule.

The coordinates are shown in Figure 6.4 for an instant in time when the molecular axis lags behind the rotating reference axis. The reference axis rotates with the constant velocity  $\Phi_x$ , and viewed

relative to this axis the molecule performs angular vibrations.

Because the two oscillations are in phase the quantities  $\Psi_x$  and  $p_{\Psi_x}$  will depend only on the linear displacement  $x$ .

Using equations (6.2) and (6.3) it is possible to transform from the phase space coordinates  $\underline{p}_\theta, \underline{\theta}$  used in equation (6.1) to the new angular coordinates  $\underline{p}_\Phi, \underline{\Phi}$ , so that

$$\langle V_x(0)V_x(t) \rangle = \frac{\int \dots \int V_x(0)V_x(t) e^{-H/kT} d\underline{p}_{r_1} \dots d\underline{r}_N d\underline{p}_{\Phi_1} \dots d\underline{\Phi}_N}{\int \dots \int e^{-H/kT} d\underline{p}_{r_1} \dots d\underline{r}_N d\underline{p}_{\Phi_1} \dots d\underline{\Phi}_N} \quad (6.4)$$

where  $H = H(\underline{p}_r, \underline{r}, \underline{p}_\Phi, \underline{\Phi})$

and it is noted that for coordinate transformation in phase space the Jacobian is unity (114). In practice the above transformation requires knowledge of the functions  $\Psi_x(x)$  and  $p_{\Psi_x}(x)$ . Expressions for these quantities are obtained below.

For small oscillations the total potential energy can be expressed in terms of a Taylor's series expansion as

$$U(x, \Psi_x) = U(0,0) + \left( \frac{\partial U}{\partial x} \right)_{\substack{x=0 \\ \Psi_x=0}} x + \left( \frac{\partial U}{\partial \Psi_x} \right)_{\substack{x=0 \\ \Psi_x=0}} \Psi_x + \frac{1}{2} \left( \frac{\partial^2 U}{\partial x^2} \right)_{\substack{x=0 \\ \Psi_x=0}} x^2 \\ + \left( \frac{\partial^2 U}{\partial x \partial \Psi_x} \right)_{\substack{x=0 \\ \Psi_x=0}} x \Psi_x + \frac{1}{2} \left( \frac{\partial^2 U}{\partial \Psi_x^2} \right)_{\substack{x=0 \\ \Psi_x=0}} \Psi_x^2 + \dots \quad (6.5)$$

Since  $U(x, \Psi_x)$  is a minimum at  $x = 0$  and  $\Psi_x = 0$

$$\left( \frac{\partial U}{\partial x} \right)_{\Psi_x=0} = \left( \frac{\partial U}{\partial \Psi_x} \right)_{\Psi_x=0} = 0 \quad (6.6)$$

Neglecting terms higher than second order, we have

$$\begin{aligned} U(x, \Psi_x) = U(0,0) + \frac{1}{2} \left( \frac{\partial^2 U}{\partial x^2} \right)_{x=0} x^2 + \left( \frac{\partial^2 U}{\partial x \partial \Psi_x} \right)_{\Psi_x=0} x \Psi_x \\ + \frac{1}{2} \left( \frac{\partial^2 U}{\partial \Psi_x^2} \right)_{\Psi_x=0} \Psi_x^2 \end{aligned} \quad (6.7)$$

Denoting

$$k_{11} = \left( \frac{\partial^2 U}{\partial x^2} \right)_{\Psi_x=0} \quad (6.8)$$

$$k_{12} = \left( \frac{\partial^2 U}{\partial x \partial \Psi_x} \right)_{\Psi_x=0} \quad (6.9)$$

$$k_{22} = \left( \frac{\partial^2 U}{\partial \Psi_x^2} \right)_{\Psi_x=0} \quad (6.10)$$

equation (6.7) can be written as

$$U(x, \Psi_x) = U(0,0) + \frac{1}{2} k_{11} x^2 + k_{12} x \Psi_x + \frac{1}{2} k_{22} \Psi_x^2 \quad (6.11)$$

For small oscillations the total kinetic energy may be written as

$$K = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} I \dot{\Psi}_x^2 \quad (6.12)$$

where  $\dot{x} = \frac{dx}{dt}$  and  $\dot{\Psi}_x = \frac{d\Psi}{dt}$ , and the Lagrangian of the system becomes

$$\begin{aligned} L = K(\dot{x}, \dot{\Psi}_x) - U(x, \Psi_x) \\ = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} I \dot{\Psi}_x^2 - [U(0,0) + \frac{1}{2} k_{11} x^2 + k_{12} x \Psi_x \\ + \frac{1}{2} k_{22} \Psi_x^2] \end{aligned} \quad (6.13)$$

The Lagrangian equation of motion with respect to  $x$  is given by

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{x}} \right) = \frac{\partial L}{\partial x} \quad (6.14)$$

So that from equation (6.13)

$$m\ddot{x} + k_{11}x + k_{12}\dot{\Psi}_x = 0 \quad (6.15)$$

Similarly the Lagrangian equation of motion with respect to  $\dot{\Psi}_x$  is

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{\Psi}_x} \right) = \left( \frac{\partial L}{\partial \Psi_x} \right) \quad (6.16)$$

or

$$I\ddot{\Psi}_x + k_{22}\dot{\Psi}_x + k_{12}x = 0 \quad (6.17)$$

Let

$$x = A'\cos\omega_1 t + A''\sin\omega_1 t \quad (6.18)$$

and

$$\dot{\Psi}_x = B'\cos\omega_1 t + B''\sin\omega_1 t \quad (6.19)$$

be the solutions to equations (6.15) and (6.17). A complete solution of equations (6.15) and (6.17) is shown in Appendix 3. Differentiating equations (6.18) and (6.19) twice with respect to time yields

$$\begin{aligned} \ddot{x} &= -\omega_1^2 [A'\cos\omega_1 t + A''\sin\omega_1 t] \\ &= -\omega_1^2 x \end{aligned} \quad (6.20)$$

and

$$\begin{aligned} \ddot{\Psi}_x &= -\omega_1^2 [B'\cos\omega_1 t + B''\sin\omega_1 t] \\ &= -\omega_1^2 \dot{\Psi}_x \end{aligned} \quad (6.21)$$

Substituting equations (6.20) and (6.21) into equations (6.15) and



(6.17)

$$-\omega_1^2 mx + k_{11}x + k_{12}\Psi_x = 0 \quad (6.22)$$

$$-\omega_1^2 I\Psi_x + k_{22}\Psi_x + k_{12}x = 0 \quad (6.23)$$

Eliminating  $\omega_1^2$  and rearranging we have

$$\frac{I\Psi_x^2}{mx^2} [k_{11}x^2 + k_{12}x\Psi_x] = [k_{22}\Psi_x^2 + k_{12}x\Psi_x] \quad (6.24)$$

The potential energy  $U(x, \Psi_x)$  now becomes

$$\begin{aligned} U(x, \Psi_x) &= U(0,0) + \frac{1}{2} [k_{11}x^2 + k_{12}x\Psi_x] + \frac{1}{2} [k_{22}\Psi_x^2 + k_{12}x\Psi_x] \\ &= U(0,0) + \left[ \frac{I\Psi_x^2}{mx^2} + 1 \right] \frac{1}{2} [k_{11}x^2 + k_{12}x\Psi_x] \end{aligned} \quad (6.25)$$

Let us consider at any time  $t = t_0$ ,  $x = 0$  and  $\Psi_x = 0$ , then

$$0 = A' \cos \omega_1 t_0 + A'' \sin \omega_1 t_0 \quad (6.26)$$

$$\frac{A''}{A'} = -\cot \omega_1 t_0 \quad (6.27)$$

and

$$0 = B' \cos \omega_1 t_0 + B'' \sin \omega_1 t_0 \quad (6.28)$$

or

$$\frac{B''}{B'} = -\cot \omega_1 t_0 \quad (6.29)$$

therefore

$$\frac{A''}{A'} = \frac{B''}{B'} \quad (6.30)$$

Combining equations (6.18) and (6.19) we have

$$\Psi_x = \frac{B' \cos \omega_1 t + B'' \sin \omega_1 t}{A' \cos \omega_1 t + A'' \sin \omega_1 t} x$$

$$\begin{aligned}
&= \frac{B'[\cos\omega_1 t + \frac{B''}{B'} \sin\omega_1 t]}{A'[\cos\omega_1 t + \frac{A''}{A'} \sin\omega_1 t]} x \\
&= \Xi x
\end{aligned} \tag{6.31}$$

where

$$\Xi = \frac{B'}{A'} \tag{6.32}$$

Equation (6.25) can be rewritten as

$$U(x, \Psi_x) = U(0,0) + \left[ \frac{I\Xi^2}{m} + 1 \right] \frac{1}{2} [k_{11}x^2 + k_{12}x\Psi_x] \tag{6.33}$$

Differentiating equation (6.31) with respect to time we get

$$\dot{\Psi}_x = \Xi \dot{x} \tag{6.34}$$

The total kinetic energy is given by

$$K = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} I \dot{\Psi}_x^2 \tag{6.35}$$

and making use of equation (6.32) we have

$$\begin{aligned}
K &= \frac{1}{2} m \dot{x}^2 + \frac{1}{2} I [\Xi \dot{x}]^2 \\
&= \frac{1}{2} m \dot{x}^2 \left[ \frac{I\Xi^2}{m} + 1 \right]
\end{aligned} \tag{6.36}$$

Now we define

$$c = \left[ \frac{I\Xi^2}{m} + 1 \right] \tag{6.37}$$

The moment of inertia appearing in the above equations is that for the molecule rotating about an axis fixed in space, rather than about a body axis. It may be regarded as a time-average of the principal moments of inertia for the molecule. In the limit where hindered rotation is absent, as for dilute gases and monatomic molecules at all densities,  $B'$  and  $B''$  are zero and so is  $\Xi$ , so that  $c$  reduces to unity.

The Hamiltonian for the system of  $N$  molecules in one dimension can be written as

$$H = K_{CM} + K_{\Phi} + U$$

$$= \sum_{i=1}^N \frac{cp_{ix}^2}{2m} + cU(x_1 \dots x_N) + \sum_{i=1}^N \frac{p_{\Phi i}^2}{2I} + U(0) \quad (6.38)$$

where

$$U(x_1 \dots x_N) = \frac{1}{2} \sum_{i=1}^N [k_{11}x_i^2 + k_{12}x_i\psi_{xi}] = \frac{1}{2} [k_{11} + \Xi k_{12}] \sum_{i=1}^N x_i^2$$

and  $U(0)$  is the potential energy when all molecules are at their cell centers. In the above equation  $\sum_{i=1}^N p_{ix}^2/2m$  represents the kinetic energy due to oscillations in the  $x$ -direction, and  $U(x_1 \dots x_N)$  is the potential energy associated with the linear oscillations. The term  $c$  thus accounts for energies associated with the angular vibrations. The last two terms in equation (6.38) corresponding to the  $\Phi$  coordinate are now separable, and the center of mass Hamiltonian for the one dimensional case is

$$H_x = \sum_{i=1}^N \frac{cp_{ix}^2}{2m} + cU(x_1 \dots x_N) \quad (6.39)$$

Comparison of this equation with equation (5.8) for the center of mass Hamiltonian when there is free rotation shows that the two expressions are of the same form. In fact, as far as the equations of classical mechanics are concerned, we may treat the hindered rotation case in the same way as free rotation, by replacing the usual kinetic and potential energy terms by those in equation (6.39), that is by  $\sum_{i=1}^N cp_{ix}^2/2m$  and  $cU$  respectively. The new kinetic energy term implies that momentum  $p$  should be replaced by  $c^{1/2}p$ .

Assuming the oscillation is isotropic, so that the motions of the molecule along all the 3 orthogonal coordinates are equivalent, the time correlation function can now be written as<sup>1</sup>

$$\langle V_x(0)V_x(t) \rangle = \frac{\int_{-\infty}^{+\infty} \int_0^V cV_x(0)V_x(t)e^{-H_{CM}/kT} dp_1 \dots dp_N dr_1 \dots dr_N}{\int_{-\infty}^{+\infty} \int_0^V e^{-H_{CM}/kT} dp_1 \dots dp_N dr_1 \dots dr_N} \quad (6.40)$$

$$\text{where } H_{CM} = \sum_{i=1}^{3N} \frac{cp_i^2}{2m} + cU(r_1 \dots r_N)$$

Now define the reduced temperature  $\tilde{T}^*$  as

$$\tilde{T}^* = \frac{kT}{c\epsilon} \quad (6.41)$$

where  $c$  is given by equation (6.37). Writing equation (6.40) in terms of reduced variables, yields

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<sup>1</sup>The derivation for the three-dimensional case is considered in more detail in Appendix 4.

$$\begin{aligned}
\langle v_x(0)v_x(t) \rangle &= \frac{\frac{c\epsilon}{m} \int_{-\infty}^{+\infty} \int_0^{V^*} p_x^*(0)p_x^*(t^*) \exp \left[ - \sum_{i=1}^N \frac{p_i^{*2}}{2\tilde{T}^*} \right.}{\int_{-\infty}^{+\infty} \int_0^{V^*} \exp \left[ - \sum_{i=1}^N \frac{p_i^{*2}}{2\tilde{T}^*} \right.} \\
&\quad \left. - \frac{1}{\tilde{T}^*} \sum_{i < j}^N \phi(r_{ij}^*) \right] dp_1^* \dots dr_N^*}{\int_{-\infty}^{+\infty} \int_0^{V^*} \exp \left[ - \sum_{i=1}^N \frac{p_i^{*2}}{2\tilde{T}^*} \right.} \\
&\quad \left. - \frac{1}{\tilde{T}^*} \sum_{i < j}^N \phi(r_{ij}^*) \right] dp_1^* \dots dr_N^*} = \frac{c\epsilon}{m} g(\tilde{T}^*, V^*, t^*) \quad (6.42)
\end{aligned}$$

where  $V^*$ ,  $p^*$ ,  $r^*$  and  $t^*$  are as defined in Chapter 5. The self-diffusion coefficient is given by

$$D = \frac{c\epsilon^{1/2}}{m^{1/2}} \int_0^\infty \langle v_x^*(0)v_x^*(t^*) \rangle dt^* \quad (6.43)$$

or

$$\tilde{D}^* = \tilde{D}^*(\tilde{T}^*, V^*) \quad (6.44)$$

where  $\tilde{D}^*$  is given by

$$\tilde{D}^* = \frac{D}{c\epsilon} \sqrt{\frac{m}{\epsilon}} \quad (6.45)$$

Similarly it can be shown that

$$\tilde{\eta}^* = \tilde{\eta}^*(\tilde{T}^*, V^*) \quad (6.46)$$

$$\tilde{\kappa}^* = \tilde{\kappa}^*(\tilde{T}^*, V^*) \quad (6.47)$$

$$\tilde{\lambda}^* = \tilde{\lambda}^*(\tilde{T}^*, V^*) \quad (6.48)$$

where now the reduced shear viscosity, bulk viscosity and thermal

conductivity are given by

$$\tilde{\eta}^* = \frac{\eta \sigma^2}{c \sqrt{m\epsilon}} \quad (6.49)$$

$$\tilde{\kappa}^* = \frac{\kappa \sigma^2}{c \sqrt{m\epsilon}} \quad (6.50)$$

$$\tilde{\lambda}^* = \frac{\lambda \sigma^2}{c k \sqrt{\frac{m}{\epsilon}}} \quad (6.51)$$

For dilute gases and monatomic molecules  $c$  reduces to unity and therefore equations (6.45), (6.49), (6.50) and (6.51) all reduce to the forms obtained by the simple correspondence principle derivation in equations (5.18), (5.22), (5.23) and (5.24). Thus the above is a general derivation of the correspondence principle which should apply to dilute and dense phases, and to both monatomic and polyatomic nonpolar fluids.

### 6.3 Test of Correspondence Principle for Polyatomic Molecules

Several workers (87,88) have pointed out that the corresponding states principle in its simple form does not apply to transport properties of even relatively simple polyatomic molecules, such as nitrogen and carbon monoxide, in the dense phase. Some investigators have adopted the pessimistic viewpoint that the principle is inapplicable for such fluids. In this section the modified corresponding states principle derived above is to be tested for the viscosity, thermal conductivity and self-diffusivity of polyatomic molecules over a wide range of temperature and density conditions.

To make a test of the proposed equations, reasonably accurate values of the characteristic factor  $c$  of different fluids must be

determined. This factor can be evaluated from one experimental value for any one of the transport coefficients. Saturated liquid viscosities were used to determine  $c$ , as they seem to be the most accurately measured of the transport coefficients, and are most readily available in the literature. The factor  $c$  of 25 monatomic and polyatomic molecules thus evaluated is shown in Table 6.1. A complete list of the smoothed potential parameters evaluated from Figures 5.1 and 5.2 is also included in Table 6.1. Table 6.2 gives the sources of transport property data used here to test the correspondence principle.

The viscosity data for the low boiling molecules are estimated to have a maximum disagreement between workers of approximately 8%; an exception is oxygen for which the maximum disagreement is 20%. Saturated liquid viscosity data for the hydrocarbons are primarily obtained from a single source (69) and the accuracy of these data are not made known. The high pressure viscosity data are less accurate. Thus for nitrogen at a pressure of 250 atmospheres the maximum disagreement between workers is as much as 14%, and for methane and ethane discrepancies are over 10%.

Saturated liquid thermal conductivities appear to be of quite good accuracy for most heavy fluids, being of the order 2%. However, for inert gases, for which extensive measurements have been made, discrepancies are found to be as much as 7%. Of all the three transport coefficients, self-diffusivity measurements are the least accurate. Thus the methane data reported by different workers show discrepancies as large as 18%, and for ethane differences are 20%.

TABLE 6.1  
PARAMETERS FOR CORRESPONDENCE CORRELATION OF POLYATOMIC MOLECULES

Molecule	M	c	Smoothed Potential Parameters		$T_c$ (°K)	$P_c$ (at m)	$\omega$
			$\sigma$ (Å)	$\epsilon/k$ (°K)			
CH <sub>4</sub>	16.04	0.95	3.798	149.5	190.7	45.8	0.013
CD <sub>4</sub>	20.07	0.94	3.798	149.5	190.7	45.8	0.013
Ne	20.18	1.00	2.788	35.3	44.5	26.9	0.000
CO	28.01	1.06	3.725	101.7	133.0	34.5	0.041
N <sub>2</sub>	28.02	1.07	3.702	96.5	126.2	33.5	0.04
C <sub>2</sub> H <sub>6</sub>	30.07	1.06	4.476	220.2	305.4	48.2	0.105
O <sub>2</sub>	32.00	0.95	3.444	120.6	154.8	50.1	0.021
F <sub>2</sub>	38.00	1.08	3.340	103.0	144.0	55.0	0.115
Ar	39.94	1.00	3.453	119.8	151.0	48.0	0.00
CO <sub>2</sub>	44.01	1.24	4.018	194.7	304.2	72.9	0.225
C <sub>3</sub> H <sub>8</sub>	44.09	1.18	5.059	255.2	369.9	42.0	0.152



TABLE 6.1 (Continued)

Molecule	M	$\epsilon$	Smoothed Potential Parameters $\sigma(\text{\AA})$	$T_c$ ( $^{\circ}\text{K}$ )	$P_c$ (at m)	$\omega$
n-C <sub>4</sub> H <sub>10</sub>	58.12	1.26	5.573	425.2	37.5	0.202
i-C <sub>4</sub> H <sub>10</sub>	58.12	1.27	5.559	408.1	36.0	0.192
cyclo-pen- tane	70.13	1.35	5.577	511.8	44.6	0.193
n-C <sub>5</sub> H <sub>12</sub>	72.15	1.34	6.081	469.5	33.3	0.252
C(CH <sub>3</sub> ) <sub>4</sub>	72.15	1.41	5.926	433.8	31.6	0.195
C <sub>6</sub> H <sub>6</sub>	78.11	1.38	5.638	562.1	48.6	0.215
Kr	83.70	1.00	3.696	209.4	54.3	0.00
cyclo-hexane	84.16	1.48	5.928	553.2	40.0	0.186
n-C <sub>6</sub> H <sub>14</sub>	86.17	1.46	6.545	507.3	29.9	0.299
n-C <sub>7</sub> H <sub>16</sub>	100.20	1.59	6.983	540.3	27.0	0.352
n-C <sub>8</sub> H <sub>18</sub>	114.22	1.71	7.416	568.6	24.6	0.395
n-C <sub>9</sub> H <sub>20</sub>	128.25	1.83	7.828	594.6	22.5	0.434
Xe	131.30	1.00	4.031	289.75	58.0	0.00
CCl <sub>4</sub>	153.84	1.38	5.735	556.4	45.0	0.202

TABLE 6.2  
SOURCES OF TRANSPORT PROPERTY DATA

<u>Molecule</u>	$\eta$ <u>Reference</u>	$\lambda$ <u>Reference</u>	D <u>Reference</u>
CH <sub>4</sub>	52,64,68,69, 115,116,117, 118,119	17,27,66,138, 139,140,141	18,58,72
CD <sub>4</sub>	64		
Ne	61,62,90, 107	66,103,111	
CO	64,67,117, 120	27,66,138	71
N <sub>2</sub>	49,61,64, 67,68,98, 108,116,121, 122	27,66,100, 101,102,142, 143,144	
C <sub>2</sub> H <sub>6</sub>	69,119,123, 124	140,145	149,150
O <sub>2</sub>	59,64,67,68, 70,104,108, 120,121,125	66,146	
F <sub>2</sub>	66		
Ar	15,48,60,61, 64,65,67,97, 98,99,104, 105,108	17,27,60,66, 100,101,102, 109	18
CO <sub>2</sub>	53,104,126	138,146,139, 147	151,152,153
C <sub>3</sub> H <sub>8</sub>	52,69,118, 119,124,127, 128,129		
n-C <sub>4</sub> H <sub>10</sub>	69,130	148	

TABLE 6.2 (Continued)

<u>Molecule</u>	$\eta$ <u>Reference</u>	$\lambda$ <u>Reference</u>	D <u>Reference</u>
i-C <sub>4</sub> H <sub>10</sub>	131		
O-C <sub>5</sub> H <sub>10</sub>	69		
n-C <sub>6</sub> H <sub>12</sub>	69,130		154,155
C(CH <sub>3</sub> ) <sub>4</sub>	128,130,132, 133		156,157
C <sub>6</sub> H <sub>6</sub>	55,69,134 135	27,136,147	156,158,159, 160,161,162
Kr	33,64,65	17,60,100	18
O-C <sub>6</sub> H <sub>12</sub>	69	29,147	156,161,163
n-C <sub>6</sub> H <sub>14</sub>	69,130		
n-C <sub>7</sub> H <sub>16</sub>	69,130		
n-C <sub>8</sub> H <sub>18</sub>	69,130		
n-C <sub>9</sub> H <sub>20</sub>	69		
Xe	64,65,106	17,60,100	18,57
CCl <sub>4</sub>	29,55,128, 134,136,137	27,136,146	163,164,165

Figure 6.5 is a reduced plot of saturated liquid viscosity as a function of temperature using the improved correspondence principle, where the viscosity and temperature are now reduced according to equations (6.49) and (6.41) respectively. For clarity, only representative molecules of different molecular structures and weights are included in this figure. However, similar agreement is found for the other molecules listed in Table 6.1. The molecules used to test the modified correspondence principle include long-chain molecules such as nonane, spherical molecules such as neopentane, flat molecules such as benzene, very light molecules such as methane and neon, heavy molecules such as carbon tetrachloride and isotopic molecules such as tetradeuteromethane.

Figure 6.6 is a similar plot for reduced saturated liquid thermal conductivity. The thermal conductivity is reduced according to equation (6.51). Good agreement is found except for the data of carbon tetrachloride, benzene and neon. The deviation for neon may be due to quantum effects as has been pointed out in the previous chapter. The poor correlation for carbon tetrachloride and benzene may be due to the Eucken effect. This effect appears to be more important in the gaseous state than for liquids, and is discussed in more detail later.

Figure 6.7 is a plot of reduced self-diffusion coefficient for saturated liquids. The correlation is seen to be poorer than for the other two transport coefficients. This may be due to experimental inaccuracies.

Figure 6.8 shows a test of the principle for viscosity over a very wide range of temperatures and pressures. Pressures up to almost

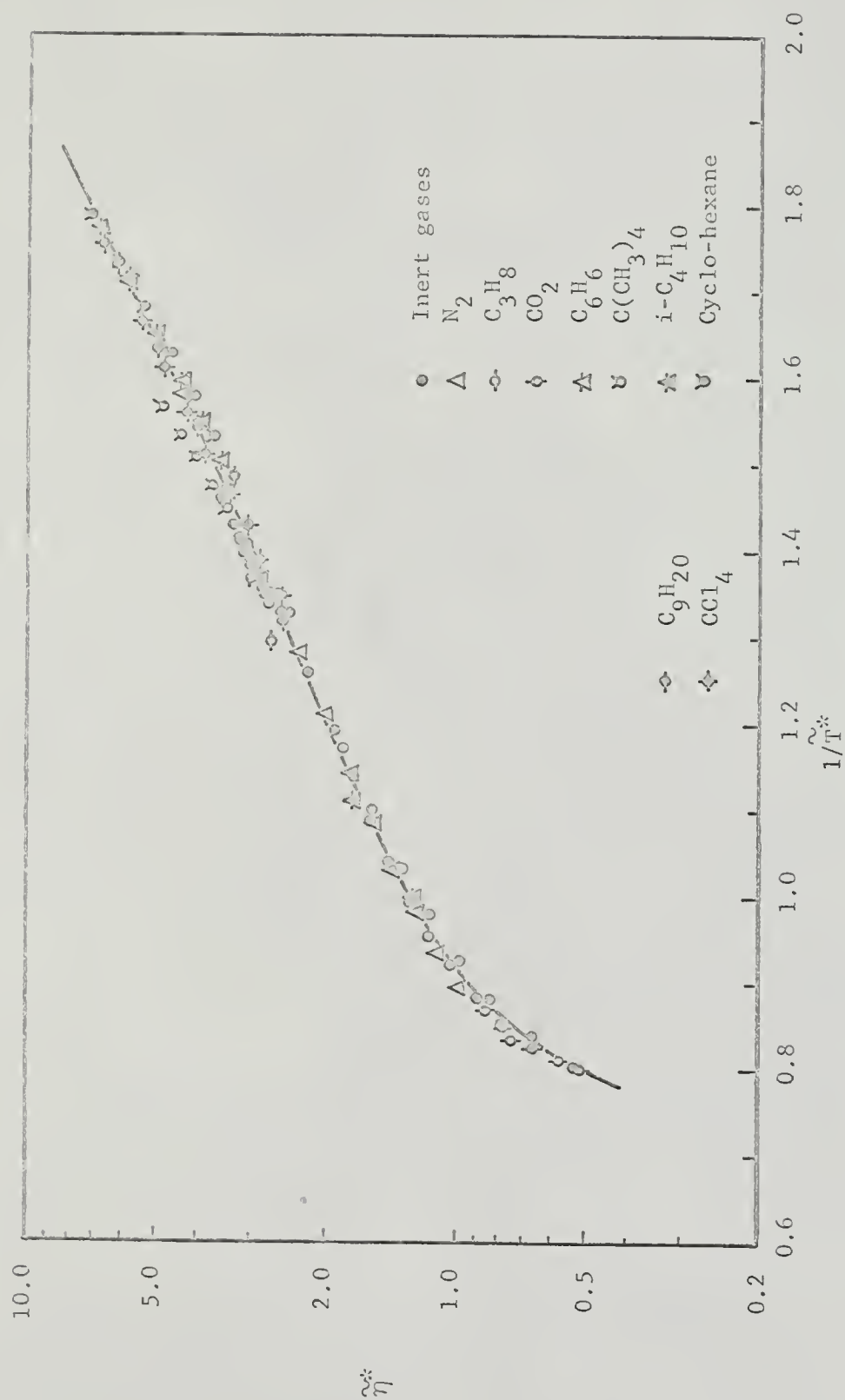


Figure 6.5. Improved Correspondence Principle for Saturated Liquid Viscosity - Polyatomic Molecules.

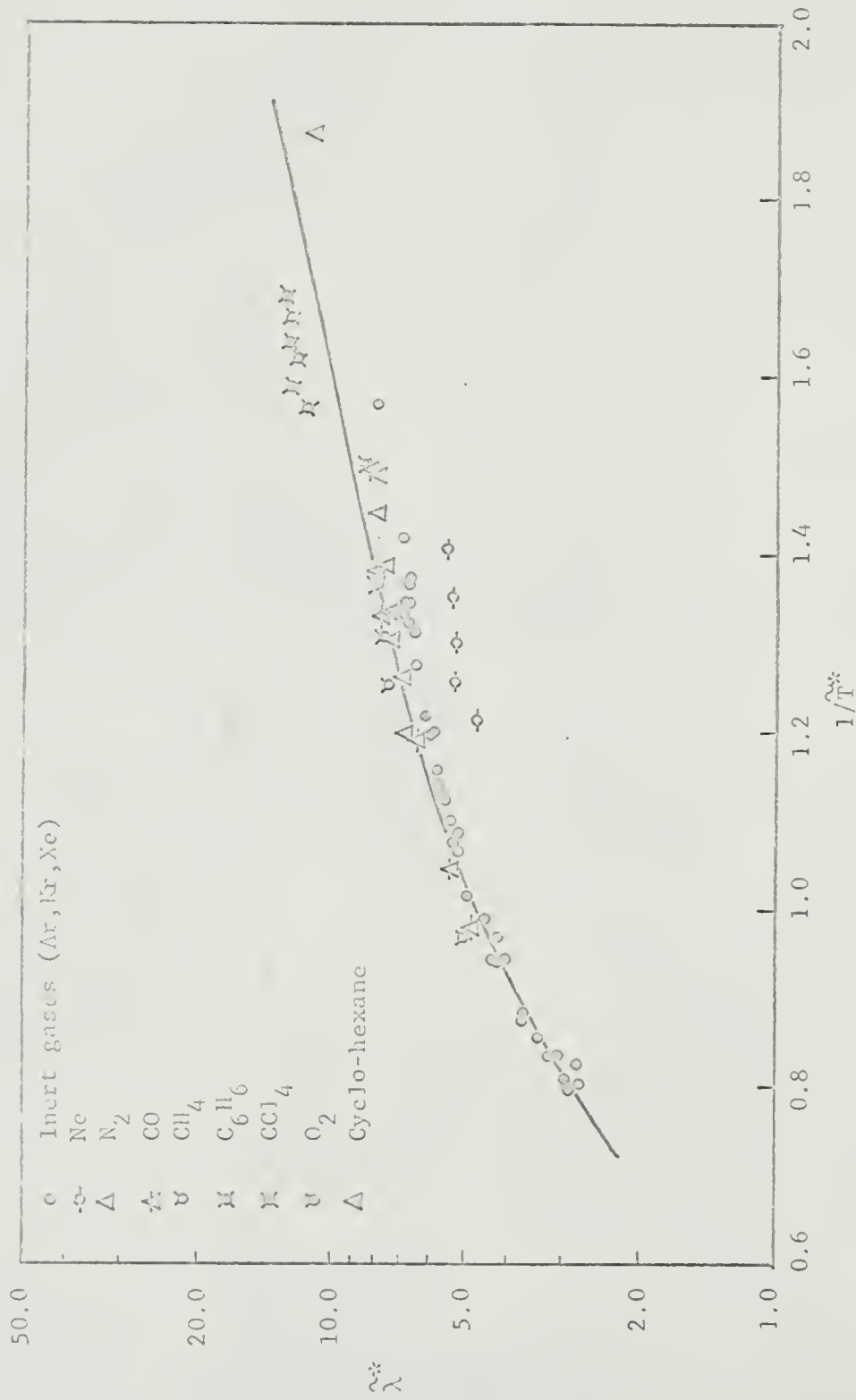


Figure 6.6. Improved Correspondence Principle for Saturated Liquid Thermal Conductivity - Polyatomic Molecules.

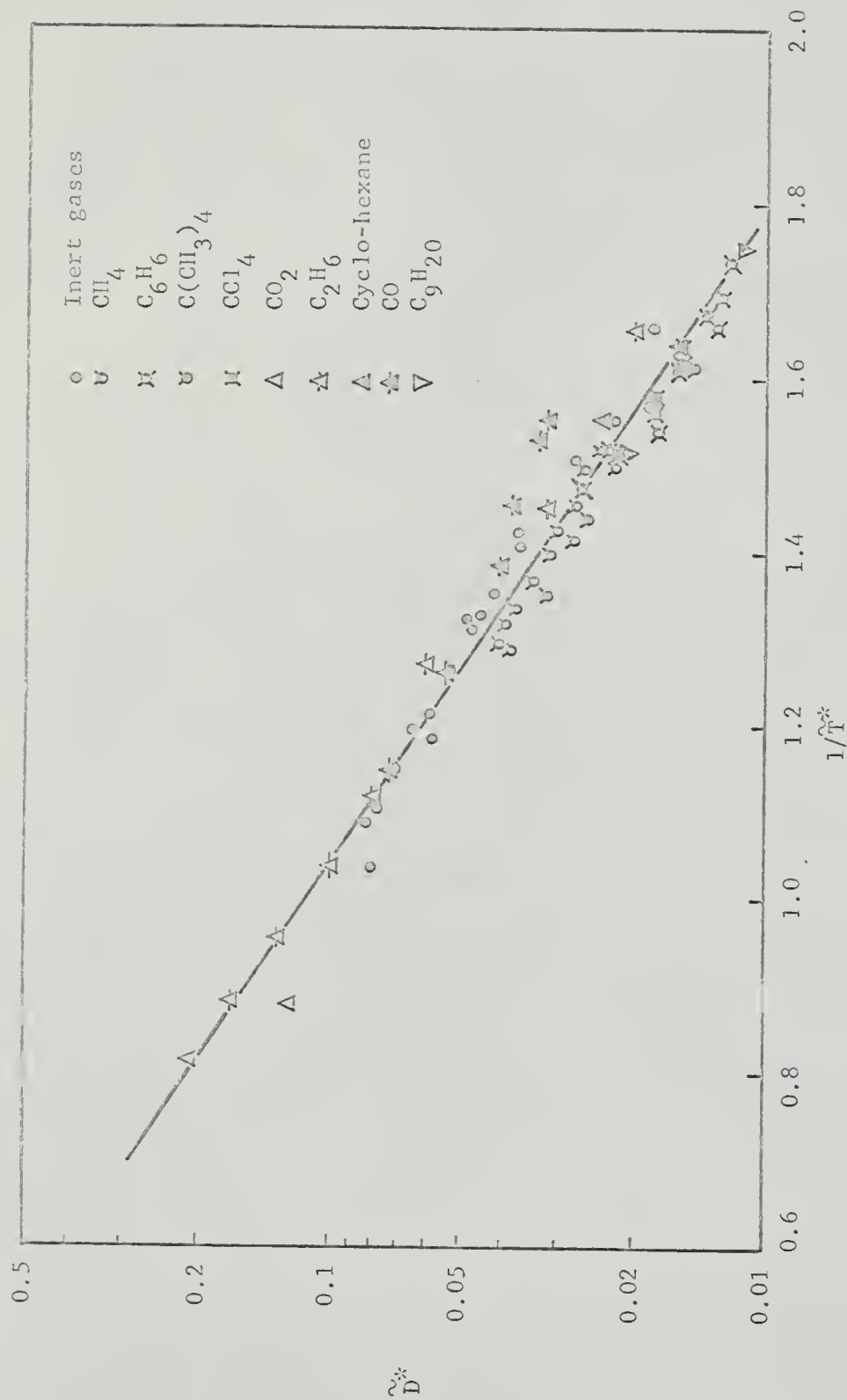


Figure 6.7. Improved Correspondence Principle for Saturated Liquid Self-Diffusivity - Polyatomic Molecules.

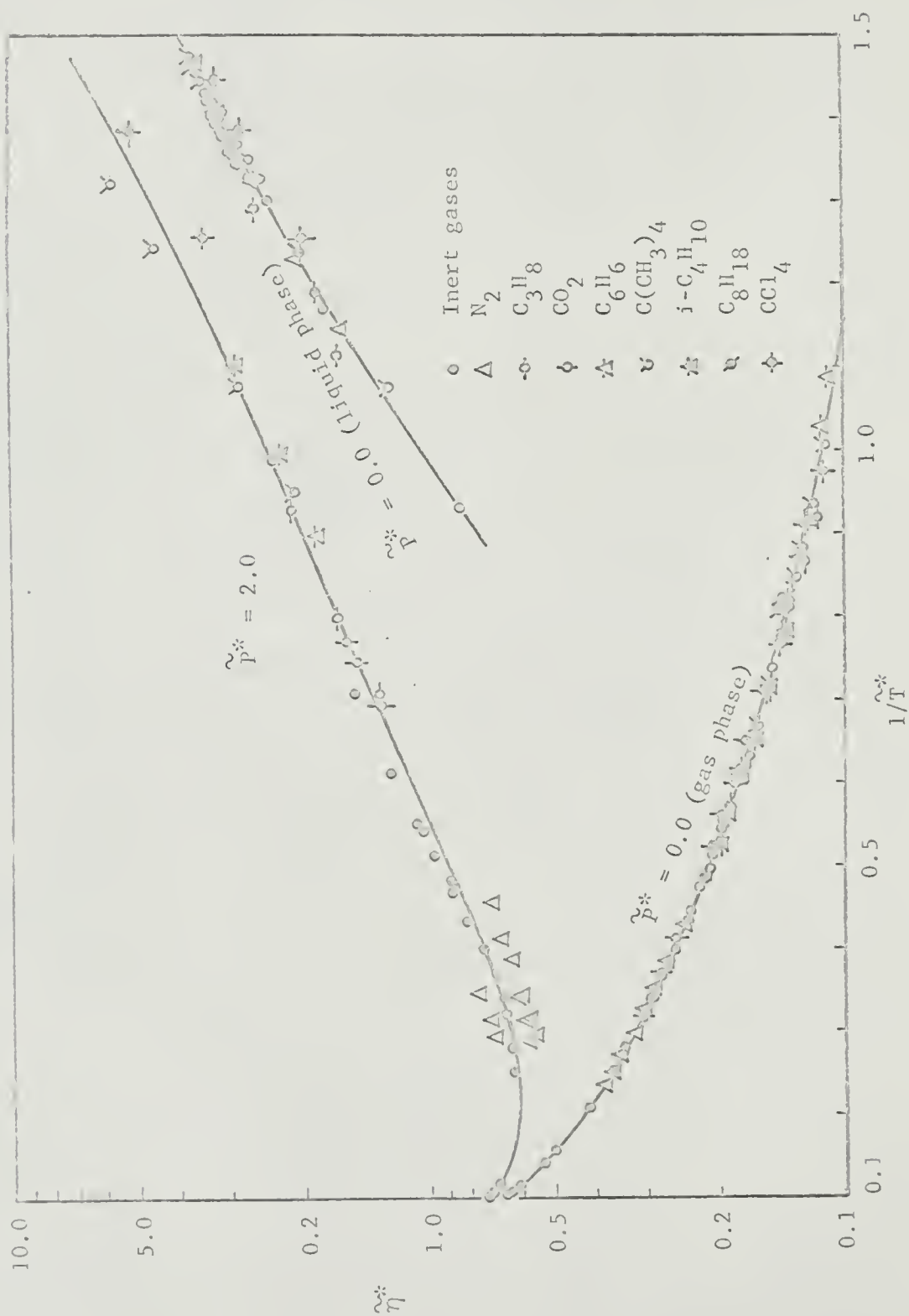


Figure 6.8. Test of Improved Correspondence Principle for High Pressure Viscosity.



1000 atmospheres are included. With the modified principle good correlation is observed for the gas and liquid viscosities at  $\tilde{P}^* = 0.1$ .<sup>1</sup> However, the correlation is poorer at higher reduced pressures. This may be due to the fact that  $c$  is slightly density dependent. Within the normal liquid density range the factor  $c$  is found to be approximately constant.

The simple correspondence principle does not apply to the thermal conductivity of polyatomic fluids in the gas phase, because of the Eucken effect. The Eucken effect can be largely corrected for by plotting the gas thermal conductivity as  $\log \tilde{\lambda}^*/\tilde{\lambda}_0^*$  vs.  $\tilde{T}^{*-1}$ , where  $\tilde{\lambda}_0^*$  is arbitrarily chosen as the value of  $\tilde{\lambda}^*$  at  $\tilde{T}^* = 0.1$ . Figure 6.9 shows such a plot for a number of monatomic and polyatomic molecules. Using this method of presentation, corresponding states correlations are found to be greatly improved. It seems that the Eucken effect is more important in the gas than in the liquid phase, for good correlation is observed in the liquid phase (with the exception of benzene and carbon tetrachloride) without correction for the effect. A test of the modified principle for the thermal conductivity of polyatomic molecules at  $\tilde{P}^* = 0.0$  (liquid phase) and  $\tilde{P}^* = 1.0$  is shown in Figure 6.10.

Tables 6.3, 6.4 and 6.5 give the coefficients of the equations (5.42), (5.43) and (5.44) fitted for the curves shown in Figures 6.5, 6.6 and 6.7 respectively. Estimated average percent errors for these equations are also given in the tables. Table 6.6 gives the coeffi-

<sup>1</sup>The reduced pressure  $\tilde{P}^*$  used for polyatomic molecules differs from that used in Chapter 5, and is defined by equation (6.62). It involves the term  $c$ . This definition arises for the equation of state, and is discussed in the next section.

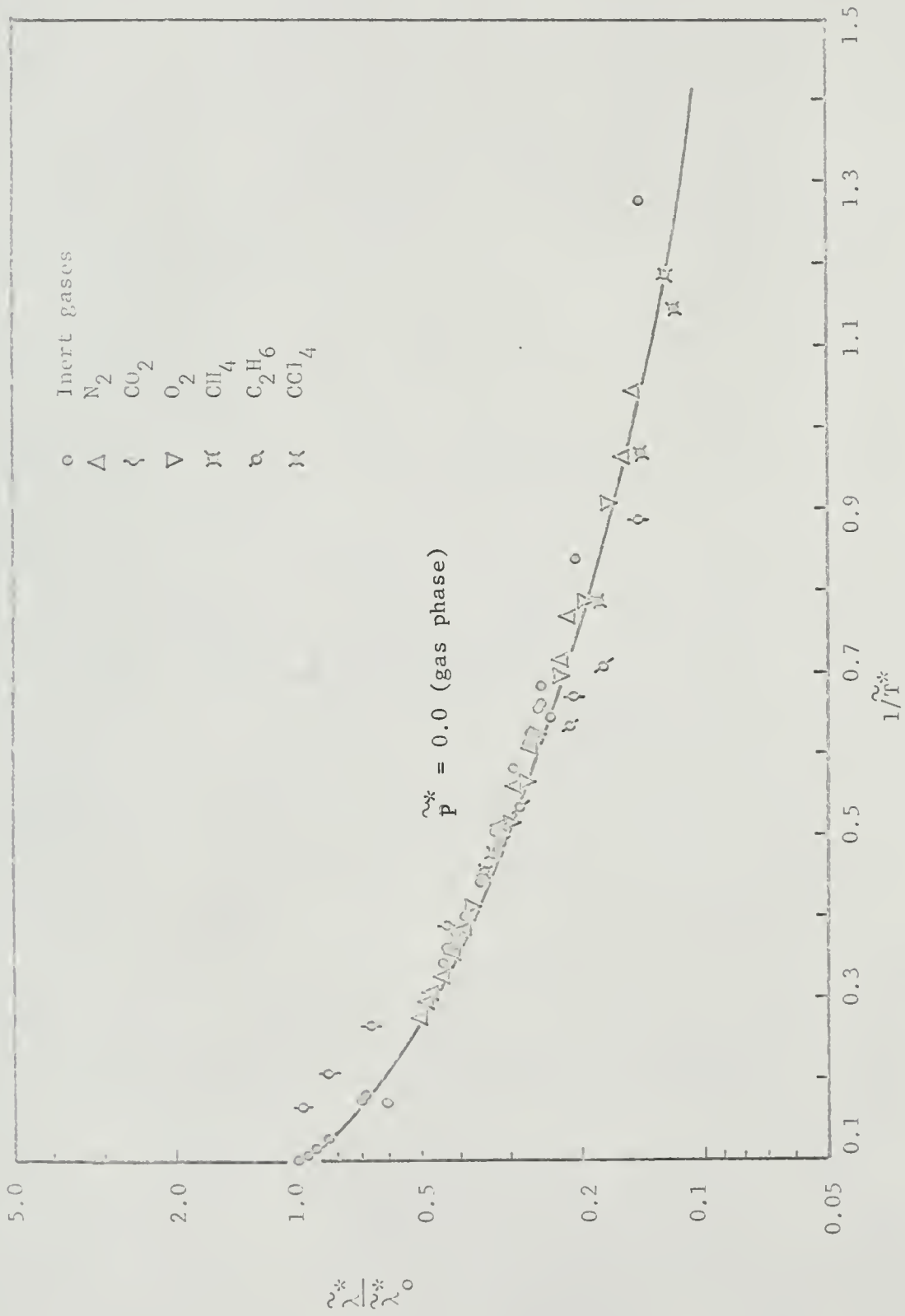


Figure 6.9. Test of Improved Correspondence Principle for Gas Thermal Conductivity - Polyatomic Molecules.

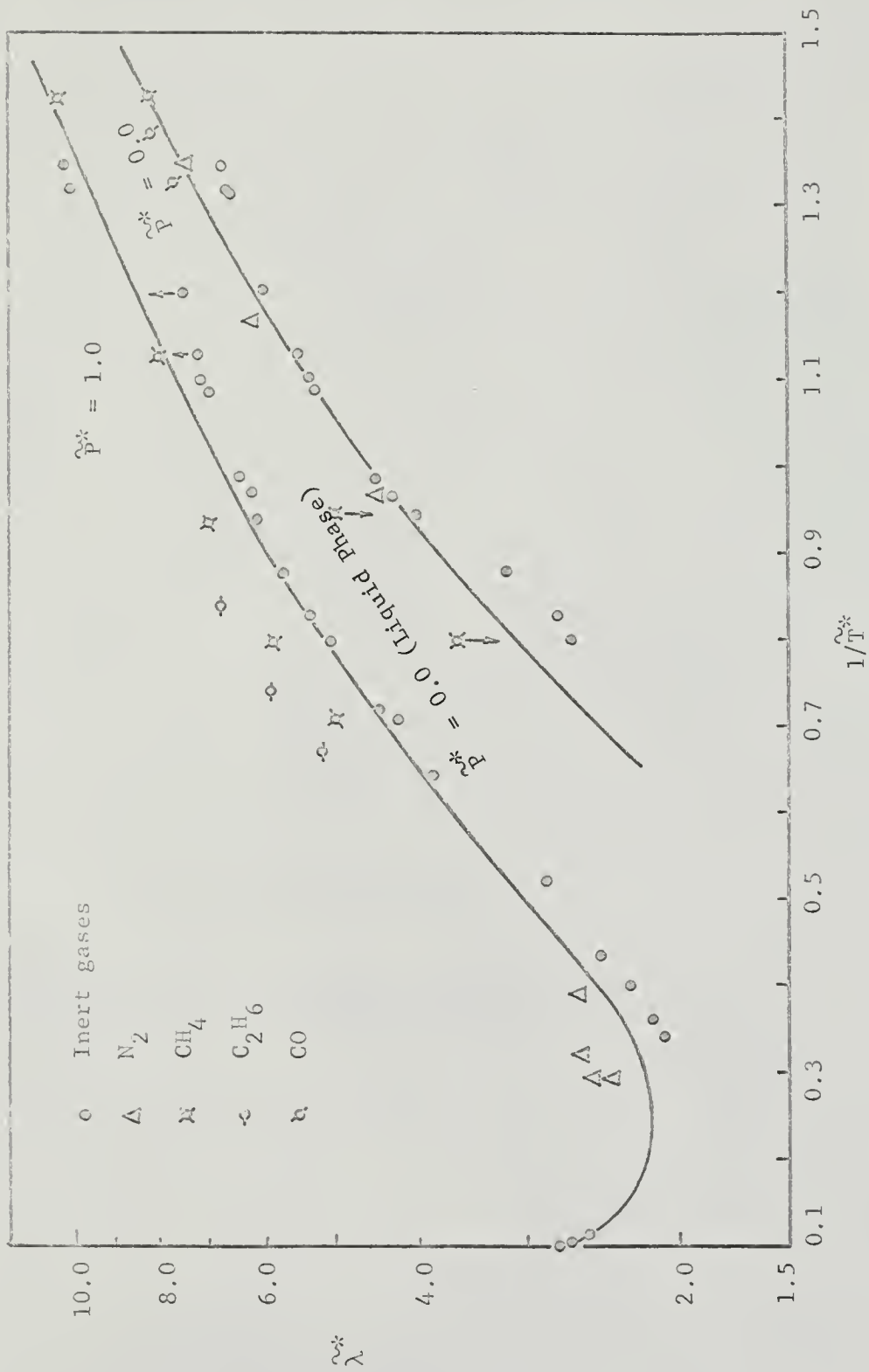


Figure 6.10. Test of Improved Correspondence Principle for High Pressure Thermal Conductivity.

TABLE 6.3

COEFFICIENTS OF SATURATED LIQUID VISCOSITY EQUATION FOR  
POLYATOMIC MOLECULES

$$\ln \eta^* = a_1 + a_2 T^{*-1} + a_3 T^{*-2} + a_4 T^{*-3} + a_5 T^{*-4}$$

Molecule	Viscosity Reference	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	Number of Points	Average % Error Y
Ar	60, 61, 64, 67, 97, 98, 99	-2.0642	-0.1432	4.7116	-2.8926	0.5530	13	6.6
Kr	64						9	1.2
Xe	64						6	0.1
Ne	61, 62						11	7.2
N <sub>2</sub>	61, 64, 67, 68, 98, 108, 121						11	9.5
O <sub>2</sub>	64, 67, 68, 70, 120, 125						4	4.7
CO	64, 67, 120						7	1.6
F <sub>2</sub>	66						9	2.7
CH <sub>4</sub>	64, 68, 69, 115						8	7.4
CO <sub>2</sub>	53						6	12.2
CCl <sub>4</sub>	136						11	10.7

TABLE 6.3 (Continued)

Molecule	Viscosity Reference	<u>a<sub>1</sub></u>	<u>a<sub>2</sub></u>	<u>a<sub>3</sub></u>	<u>a<sub>4</sub></u>	<u>a<sub>5</sub></u>	Number of Points	Average % Error Y
C(CH <sub>3</sub> ) <sub>4</sub>	132						10	7.1
Cyclo- pentane	69						9	4.4
Cyclo- hexane	69						4	8.1
C <sub>6</sub> H <sub>6</sub>	69						6	7.1
C <sub>2</sub> H <sub>6</sub>	69						6	9.8
C <sub>3</sub> H <sub>8</sub>	69						6	5.2
i-C <sub>4</sub> H <sub>10</sub>	131						2	9.2
CD <sub>4</sub>	64						8	2.2
C <sub>4</sub> H <sub>10</sub>	69						8	2.7
C <sub>5</sub> H <sub>12</sub>	69						7	2.7
C <sub>6</sub> H <sub>14</sub>	69						6	1.9
C <sub>7</sub> H <sub>16</sub>	69						7	3.2
C <sub>8</sub> H <sub>18</sub>	69						7	4.7
C <sub>9</sub> H <sub>20</sub>	69						7	5.6

Overall Y = 6.4%

TABLE 6.4

COEFFICIENTS OF SATURATED LIQUID THERMAL CONDUCTIVITY EQUATION  
FOR POLYATOMIC MOLECULES

$$\ln \lambda^* = b_1 + b_2 T^{*-1} + b_3 T^{*-2} + b_4 T^{*-3} + b_5 T^{*-4}$$

Molecule	Thermal Conductivity Reference	$b_1$	$b_2$	$b_3$	$b_4$	$b_5$	Number of Points	Average % Error Y
Ar	17,27,60, 66,100,101, 102	-2.9346	7.7058	-3.9821	0.8207	-0.0650	24	7.2
Kr	17,60,100						6	8.1
Xe	17,60,100						7	7.2
N <sub>2</sub>	27,66						15	5.6
CO	27,66						7	6.8
CH <sub>4</sub>	27,66						7	15.8
O <sub>2</sub>	66						3	16.8

Overall Y = 8.8%

TABLE 6.5

COEFFICIENTS OF SATURATED LIQUID SELF-DIFFUSIVITY EQUATION  
FOR POLYATOMIC MOLECULES

$$1nD^* = d_1 + d_2 \frac{\Delta T}{T^2}$$

Molecule	Viscosity Reference	$d_1$	$d_2$	Number of Points	Average % Error Y
Ar	18	0.6568	-2.9190	5	15.1
Kr	18			5	13.5
Xe	18, 57			6	9.7
CH <sub>4</sub>	18, 58, 72			13	7.2
CO <sub>2</sub>	151, 152, 153			2	19.4
CCl <sub>4</sub>	163, 164, 165			9	10.4
C(CH <sub>3</sub> ) <sub>4</sub>	156, 157			3	12.9
CO	71			4	47.9
C <sub>6</sub> H <sub>6</sub>	156, 158, 159, 160, 161, 162			20	7.0
Cyclo-hexane	156, 161, 163			4	10.0
C <sub>2</sub> H <sub>6</sub>	149, 150			7	33.0
C <sub>5</sub> H <sub>12</sub>	154, 155			6	8.3
C <sub>6</sub> H <sub>14</sub>	154, 155			2	8.4
C <sub>7</sub> H <sub>16</sub>	154, 155			8	13.8

TABLE 6.5 (Continued)

Molecule	Viscosity Reference	d <sub>1</sub>	d <sub>2</sub>	Number of Points	Average % Error Y
C <sub>8</sub> H <sub>18</sub>	154, 155			2	17.4
C <sub>9</sub> H <sub>20</sub>	154, 155			2	6.4



TABLE 6.6  
COEFFICIENTS OF HIGH PRESSURE VISCOSITY EQUATIONS  
FOR POLYATOMIC MOLECULES

Molecule	Reduced Pressure $P^*$	Reduced Temp. Range	$\ln \eta^* = a_1 + a_2 T^{*-1} + a_3 T^{*-2} + a_4 T^{*-3} + a_5 T^{*-4}$					Number of Points	Average % Error Y
			$a_1$	$a_2$	$a_3$	$a_4$	$a_5$		
Ar, Kr, Xe, Ne, CH <sub>4</sub> , i-C <sub>4</sub> H <sub>10</sub> , CO <sub>2</sub> , N <sub>2</sub> , O <sub>2</sub> CO, CCl <sub>4</sub> , C <sub>6</sub> H <sub>6</sub> , C(CH <sub>3</sub> ) <sub>4</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , C <sub>4</sub> H <sub>10</sub> , C <sub>5</sub> H <sub>12</sub> , C <sub>6</sub> H <sub>14</sub> , C <sub>7</sub> H <sub>16</sub> , C <sub>8</sub> H <sub>18</sub>	0.0 (Gas Phase)	0.7-10.0	0.0731	-5.6149	6.8692	-4.9041	1.4168	170	2.6
Ar, Kr, Xe, Ne, CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> (Liquid Phase) C <sub>3</sub> H <sub>8</sub> , N <sub>2</sub> , O <sub>2</sub> CO, CCl <sub>4</sub> , C(CH <sub>3</sub> ) <sub>4</sub> , C <sub>5</sub> H <sub>12</sub> , C <sub>6</sub> H <sub>14</sub>	0.0 (Liquid Phase)	0.4-1.0	-3.1053	2.7289	1.5729	-1.3368	0.2623	93	5.6

TABLE 6.6 (Continued)

Molecule	Reduced Pressure $p^*$	Reduced Temp. Range	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	Number of Points	Average % Error Y
Ar, Kr, Xe, Ne, CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>3</sub> H <sub>8</sub> , i-C <sub>4</sub> H <sub>10</sub> , CO <sub>2</sub> , N <sub>2</sub> , CCl <sub>4</sub> , C <sub>6</sub> H <sub>6</sub> , C(CH <sub>3</sub> ) <sub>4</sub>	1.0	0.6-10.0	0.0113	-5.9411	13.875	-9.4687	2.2121	108	8.7
Ar, Kr, Xe, Ne, C <sub>3</sub> H <sub>8</sub> , i-C <sub>4</sub> H <sub>10</sub> , CO <sub>2</sub> , N <sub>2</sub> , CCl <sub>4</sub> , C(CH <sub>3</sub> ) <sub>4</sub>	2.0	0.7-10.0	-0.0811	-3.7204	10.853	-8.5384	2.3665	42	9.1

coefficients of equations for the curves in Figure 6.8 and Tables 6.7 and 6.8 give coefficients of the thermal conductivity equations for the curves in Figures 6.9 and 6.10 respectively. A list of the values of  $\tilde{\lambda}_0^*$  for molecules considered in Figure 6.9 is also included in Table 6.7.

#### 6.4 Comparison with Theory for Thermodynamic Properties.

Recently, Hermesen and Prausnitz (166) proposed a corresponding states treatment for the thermodynamic properties of liquid hydrocarbons. Their approach was based on Prigogine's corresponding states theory for r-mers (50). They defined the reduced temperature as

$$\tilde{T} = \frac{kT}{(s/c)_k \epsilon} \quad (6.52)$$

and the reduced molal volume as

$$\tilde{V} = \frac{V}{\tilde{V}_k^*} \quad (6.53)$$

where  $\tilde{V}_k^*$  is an arbitrary characteristic volume. Potential parameters determined from second virial coefficient data as given by Hirschfelder, Curtiss and Bird (20) were used. By fitting experimental molal volume data using a high speed computer they obtained  $(s/c)_k$  and  $\tilde{V}_k^*$  for a large number of hydrocarbons. It is of interest to compare their values of  $(s/c)_k$  obtained from molal volume data with the values of  $c$  obtained here from viscosity data. These quantities, together with the potential parameters used in each case, are compared in Table 6.9. Hermesen and Prausnitz arbitrarily assumed the value of  $(s/c)_k$  for methane to be unity. After multiplying their values of  $(s/c)_k$  by a

TABLE 6.7

COEFFICIENTS OF GAS THERMAL CONDUCTIVITY EQUATION  
FOR POLYATOMIC MOLECULES

Molecule	$\lambda_o^*$	Thermal Conductivity Reference	$\ln(\lambda^*/\lambda_o^*) = b_1 + b_2 T^{*-1} + b_3 T^{*-2} + b_4 T^{*-3} + b_5 T^{*-4}$					Number of Points	Average %Error y
			$b_1$	$b_2$	$b_3$	$b_4$	$b_5$		
Ar	2.52	17, 102, 109	0.3791	-4.3084	2.8710	-0.8870	0.05747	15	9.4
Ne	2.52	66, 111						13	7.5
N <sub>2</sub>	3.4	66, 142, 143 144						17	5.2
CO <sub>2</sub>	4.4	138, 139, 146, 147						7	20.3
O <sub>2</sub>	3.4	66, 146						9	2.4
CH <sub>4</sub>	4.1	138, 139, 140						4	2.9
C <sub>2</sub> H <sub>6</sub>	7.6	140, 145						5	14.3
CCl <sub>4</sub>	9.6	146						3	9.1

Overall Y = 9.6%

TABLE 6.8

COEFFICIENTS OF HIGH PRESSURE THERMAL CONDUCTIVITY EQUATIONS  
FOR POLYATOMIC MOLECULES

Molecule	Reduced Pressure $P^*$	Reduced Temp. Range	$10^3 \lambda^* = b_1 + b_2 T^{*-1} + b_3 T^{*-2} + b_4 T^{*-3} + b_5 T^{*-4}$					Number of Points	Average % Error Y
			$b_1$	$b_2$	$b_3$	$b_4$	$b_5$		
Ar, Kr, Xe, N <sub>2</sub> , CO, CH <sub>4</sub>	0.0 (Liquid Phase)	0.6-1.2	-1.6288	3.3030	1.6104	-2.4330	0.6644	38	1.1
Ar, Kr, Xe, N <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>4</sub> H <sub>10</sub>	1.0	0.7-3.0	3.2250	-16.995	40.254	-34.739	10.262	40	14.7

TABLE 6.9

COMPARISON OF  $\epsilon$  WITH CORRESPONDING PARAMETER OF  
HERMSEN AND PRAUSNITZ (166)

Molecule	$\epsilon$	$C/k$ ( $^{\circ}\text{K}$ )	$\sigma$ $_{\text{O}}$ ( $\text{\AA}$ )	$\text{NO}$ $^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$	$\epsilon_{\text{HP}} = \left( \frac{s}{c} \right)_k$	$(\epsilon/k)_k$ ( $^{\circ}\text{K}$ )	$\sigma_k$ $_{\text{O}}$ $\text{\AA}$	$V_k^*$ $^3$ $\text{cm}^3 \cdot \text{mol}^{-1}$
$\text{CH}_4$	0.95	149.1	3.798	32.99	0.95	148.2	3.817	23.70
$\text{C}_2\text{H}_6$	1.06	220.2	4.476	54.01	1.06	200.0	3.954	33.30
$\text{C}_3\text{H}_8$	1.18	255.2	5.059	77.98	1.22	208.3	5.637	45.06
$n\text{-C}_4\text{H}_{10}$	1.26	278.9	5.573	104.25	1.42	215.4	4.971	57.42
$i\text{-C}_4\text{H}_{10}$	1.27	270.6	5.559	103.47	1.37	210.9	-	58.09
$\text{O-C}_5\text{H}_{10}$	1.35	338.8	5.577	104.47	1.44	247.6	-	58.20
$n\text{-C}_6\text{H}_{12}$	1.34	292.7	6.081	135.44	1.52	217.0	-	68.88
$\text{C}(\text{CH}_3)_4$	1.41	286.5	5.926	125.34	1.58	200.0	-	71.08
$\text{O-C}_6\text{H}_{12}$	1.48	368.4	5.928	125.47	1.54	247.6	-	68.54
$n\text{-C}_6\text{H}_{14}$	1.46	299.7	6.545	168.86	1.60	219.5	-	80.53
$\text{C}_6\text{H}_6$	1.37	364.0	5.638	107.94	1.22	310.6	6.92	56.36
$n\text{-C}_7\text{H}_{16}$	1.59	299.8	6.983	205.09	1.68	221.6	8.880	92.31
$n\text{-C}_8\text{H}_{18}$	1.71	298.9	7.416	245.65	1.76	223.0	-	104.23

constant factor chosen such that the value of  $(s/k)_k$  for methane agrees with the value of  $c$  for methane used in this work, it is seen from Table 6.9 that the two parameters are approximately the same for most hydrocarbons. This suggests that the correspondence principle should apply quite well to both transport and thermodynamic properties in the liquid phase using a single set of  $c$  values. However, it may be necessary to use different sets of potential parameters in the two cases.

It is of interest to examine the modified correspondence principle for thermodynamic properties of polyatomic fluids. From statistical thermodynamics, the pressure is given in terms of the canonical partition function as

$$P = kT \left( \frac{\partial \ln Q}{\partial V} \right)_T \quad (6.54)$$

where the partition function may be separated into a density-independent part  $Q_i$  and a part  $Q_{CM}$  which depends on density,

$$Q = \frac{1}{N!} Q_i Q_{CM} \quad (6.55)$$

where

$$Q_{CM} = \frac{1}{h^{3N}} \int_{-\infty}^{+\infty} \int_0^V e^{-H_{CM}/kT} dp_1 \dots dr_N \quad (6.56)$$

$$H_{CM} = \sum_{i=1}^{3N} \frac{c p_i^2}{2m} + cU(r_1 \dots r_N) \quad (6.57)$$

$$\text{and} \quad U(r_1 \dots r_N) = \epsilon \sum_{i < j}^N \phi \left( \frac{r_{ij}}{\sigma} \right) \quad (6.58)$$

therefore

$$P = kT \left[ \frac{\partial \left( \ln \int_0^V \dots \int_0^V e^{-cU/kT} d\mathbf{r}_1 \dots d\mathbf{r}_N \right)}{\partial V} \right]_T \quad (6.59)$$

since  $\int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} e^{-\sum_{i=1}^N \frac{cp_i^2}{2mkT}} dp_1 \dots dp_N$  is independent of density.

Equation (6.59) may be written in terms of reduced variables to give

$$P = \frac{c\epsilon}{\sigma^3} \tilde{T}^* \left[ \frac{\partial \left( \ln \int_0^{V^*} \dots \int_0^{V^*} \exp \left[ -\frac{1}{\tilde{T}^*} \sum_{i < j}^N \phi(r_{ij}^*) \right] d\mathbf{r}_1^* \dots d\mathbf{r}_N^* \right)}{\partial V^*} \right]_{T^*} \quad (6.60)$$

$$\text{or} \quad \tilde{P}^* = \tilde{P}^*(\tilde{T}^*, V^*) \quad (6.61)$$

$$\text{where} \quad \tilde{P}^* = \frac{P\sigma^3}{c\epsilon} \quad (6.62)$$

$$V^* = \frac{V}{\sigma^3} \quad (6.63)$$

Pitzer (94) has pointed out that the simple 2-parameter corresponding states law fails most noticeably for the liquid-vapor region, and suggested using experimental vapor pressure data to obtain a third parameter. Figure 6.11 shows a plot of reduced vapor pressure  $\tilde{P}^*(\tilde{T}^*)$  using the simple 2-parameter corresponding states principle; substantial deviations are seen to occur, and these are ascribed by Pitzer to acentric interactions. Figure 6.12 shows a similar plot of  $\tilde{P}^*(\tilde{T}^*)$  using the new correspondence principle, with the values of  $c$  obtained from liquid viscosity data. Potential parameters used were smoothed values from gas viscosity data. The correlation is considerably improved. Further improvement can, of course, be obtained if  $c$  and potential parameters are derived from thermodynamic data.



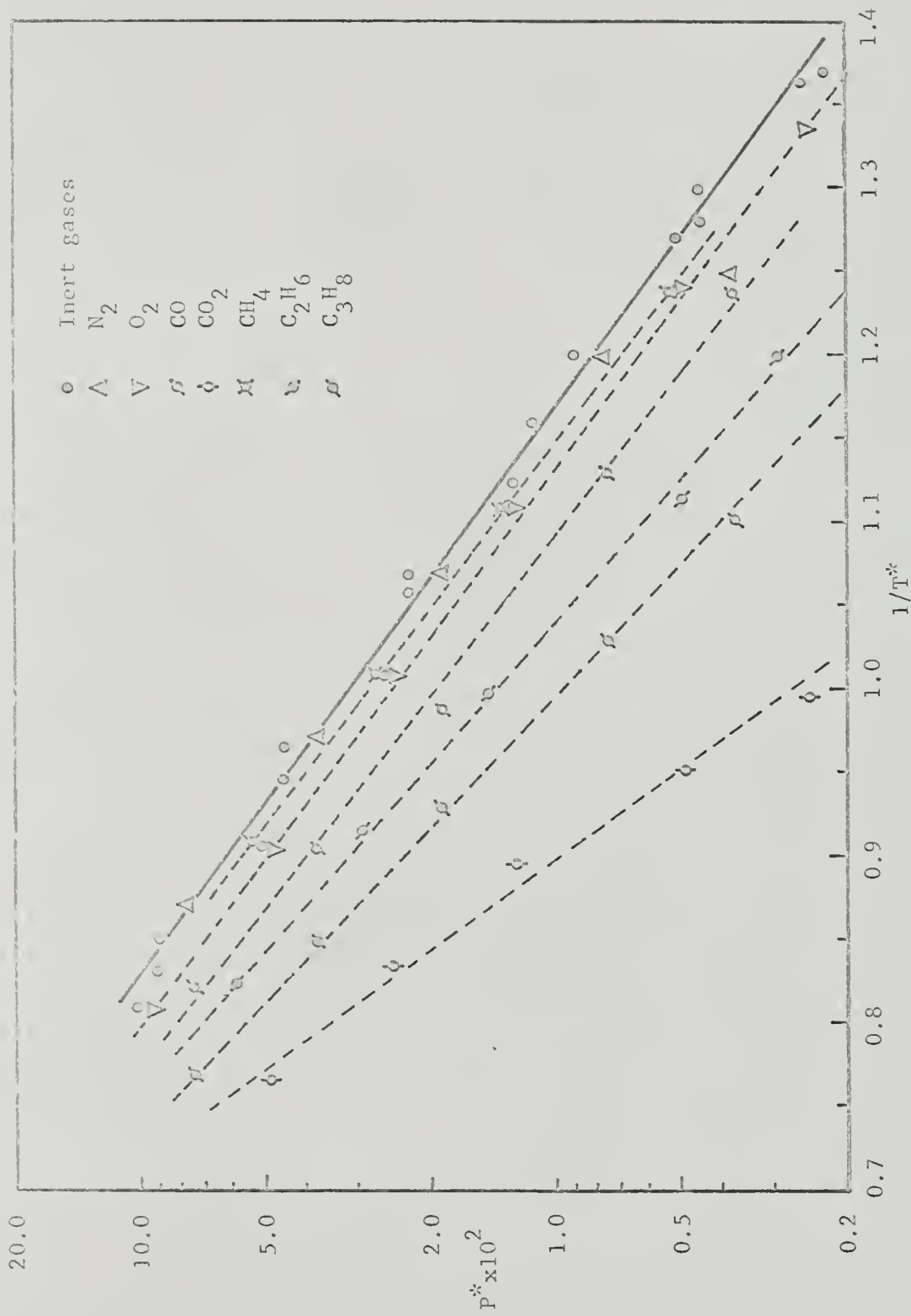


Figure 6.11. Simple Correspondence Principle - Vapor Pressure.

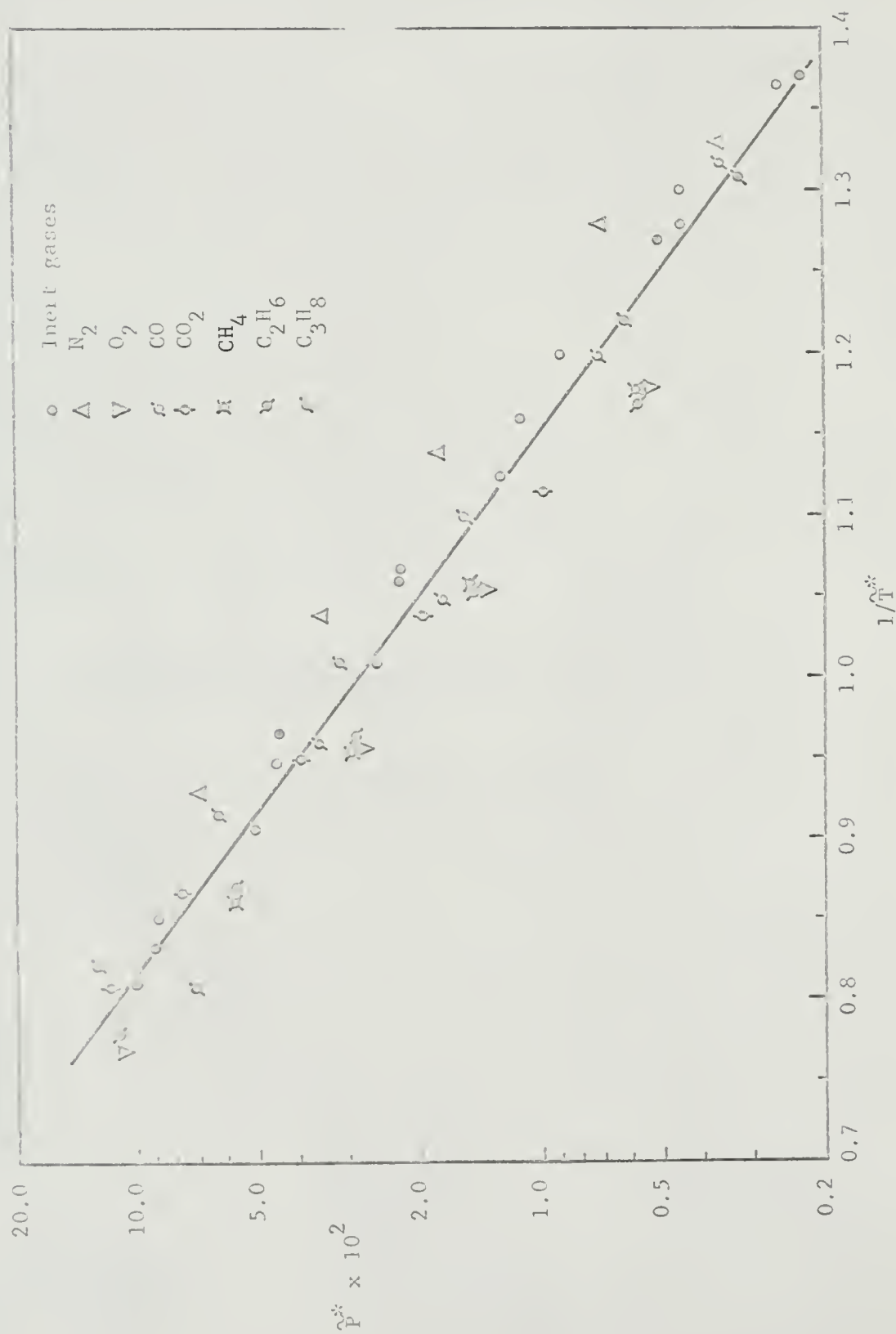


Figure 6.12. Improved Correspondence Principle - Vapor Pressure.

## CHAPTER 7

### CONCLUSIONS

The free volume equation provides a useful basis for predicting viscosities and self-diffusion coefficients of liquids at high densities, where most other correlations are unsuccessful. The fact that both  $V_O^1$  and  $E_v$  values vary in a corresponding states way indicates that the equation's success does not arise only from the availability of three adjustable parameters. The simple expressions given for  $A_O$  by Eyring and others, however, do not seem to be generally applicable. The free volume theory seems to provide somewhat more accurate values of transport properties than does the direct corresponding states approach, but has several limitations. In particular it applies only at high density ( $\rho > 2\rho_c$ ), and cannot be used to obtain thermal conductivities.

The direct corresponding states approach is of more general application, and in the form presented in Chapter 6 it may be used for all transport properties and over a wide range of densities. An attractive feature of the principle presented for polyatomic fluids is that, although a third parameter is introduced, the transport coefficients are expressed as functions of only two independent variables ( $\tilde{T}^*$  and  $\tilde{P}^*$ ). In view of the simplicity of the proposed model, it may at first sight seem somewhat surprising that the correlation is so successful. It should be remembered, however, that the model is only used to obtain the form of the reduced relationships, and not to directly calculate transport coefficients. In this

form the correspondence principle applies to a wide variety of substances, including fluids composed of relatively complex molecules which are of interest to engineers. It is easy to apply, the only parameters required for prediction being  $T_c$ ,  $P_c$ ,  $M$ ,  $\omega$  and  $c$ . The first four parameters are available in the literature, and the latter may be obtained from one experimental measurement of any one of the transport properties. When no such measurements are available it may be evaluated using thermodynamic data (e.g., vapor pressure).

In the light of the promising results of this investigation, it is felt that the free volume theory and the corresponding states principle are very useful methods for the prediction of physical properties of dense and condensed fluids. For future work the following studies are recommended.

## 7.1 Free Volume Theory

### 7.1.1 Extension to Mixtures

In the course of this work the free volume theory has been tested for the viscosity of binary mixtures of simple molecules (167). For the mixtures tested it is found that the predicted viscosity is within the experimental accuracy over the entire range of compositions. In the prediction of the mixture viscosity no mixture data are required. For future studies, the free volume theory may be extended to binary diffusion coefficients and viscosity of multicomponent systems.

### 7.1.2 Electrolyte Solutions

Podolsky (168) has utilized the Eyring cell theory to predict the self-diffusion coefficient of electrolyte solutions.

However, no attempt has yet been made to apply the free volume theory to the transport properties of electrolytes. Based on the promising results demonstrated by the free volume theory for the viscosity and self-diffusivity of pure fluids, it is believed that this theory may serve as an improved basis for predicting transport properties of electrolytes.

## 7.2 Corresponding States Principle

### 7.2.1 Mixtures

The corresponding states principle may be derived in the same manner as for pure substances, by starting with the time correlation function equations for the transport properties of mixtures (169-171).

### 7.2.2 Polar Substances

In this work only nonpolar substances are considered. It will be useful to extend the correspondence principle to polar substances. This can be done by introducing suitable reduced dipole or quadrupole moments.

### 7.2.3 Fused Salts

Transport properties of fused salts are very important for a number of practical applications. As measurements of transport properties of fused salts are difficult, it will be of interest to extend the corresponding states principle to these substances. Such liquids are composed of ions which may often be regarded as roughly spherical charged particles.

### 7.2.4 Thermodynamic Properties

A further extension of the proposed principle for polyatomic

molecules will be a detailed study of its application to thermodynamic properties in the dense and condensed phase. A preliminary study shows that the proposed correspondence principle greatly improves the correlation for vapor pressure. With suitable reduced expressions, it seems likely that the correspondence principle may apply to all other thermodynamic properties.

#### 7.2.5 Prediction of $c$

Although an approximate expression has been obtained for the factor  $c$  from the derivation of the correspondence principle for polyatomic molecules, no extensive study of the behavior of this parameter has been made. The parameter  $c$  is a function of the moment of inertia, mass and potential parameters of the molecule, as well as the density and temperature. A useful extension of this work will be the study of the properties of the parameter  $c$  and methods of predicting it. Any more detailed examination should include a study of the density dependence of this parameter.

## APPENDICES

## APPENDIX 1

### CHUNG'S DERIVATION OF THE FREE VOLUME EQUATIONS

Chung (46) considered a molecule to spend a large fraction of the time oscillating about an equilibrium position in a cell. The molecule can leave the cell to jump into a neighboring cell only when the following two events occur simultaneously: (1) a free volume greater than the minimum value  $v_0$ , which can accomodate the molecule is available, and (2) the molecule has an activation energy greater than the minimum energy barrier  $e_v$  separating two equilibrium positions.

Consider a system of  $N$  molecules. The total energy is considered to be made up of energy levels  $e_1, e_2 \dots e_j$ , such that  $N^{(1)}$  molecules are in region  $e_1$ ,  $N^{(2)}$  in  $e_2 \dots$  and so on. In addition it is assumed that a range of values of free volume  $v_1, v_2 \dots v_k$  is available to each molecule. Thus the distribution of molecules among the possible values of free volume and energy may be represented schematically by

Energy level	$e_1$	$e_2$	$e_j$
Free volume	$v_1, v_2 \dots v_k$	$v_1 v_2 \dots v_k$	$v_1 v_2 \dots v_k$
Number of molecules	$N_1^{(1)} N_2^{(1)} \dots N_k^{(1)}$	$N_1^{(2)} N_2^{(2)} \dots N_k^{(2)}$	$N_1^{(j)} N_2^{(j)} \dots N_k^{(j)}$

Thus if  $W_1$  represents the number of distinguishable ways of assigning  $N$  molecules to the different energy levels such that  $N^{(1)}$  molecules have energy  $e_1$ ,  $N^{(2)}$  have energy  $e_2 \dots$  and so on,  $W_1$  may be written



as

$$W_1 = \frac{N!}{\prod_{i=1}^j N^{(i)}!} \quad (A1.1)$$

Similarly, if  $W_2$  is the number of ways of assigning  $N_1^{(i)}$  molecules in  $v_1$ ,  $N_2^{(i)}$  in  $v_2$  ... etc., where  $i = 1$  to  $j$ , it follows that

$$\begin{aligned} W_2 &= \left[ \frac{N^{(1)}!}{\prod_{p=1}^k N_p^{(1)}!} \right] \cdots \left[ \frac{N^{(j)}!}{\prod_{p=1}^k N_p^{(j)}!} \right] \\ &= \frac{\prod_{i=1}^j N^{(i)}!}{\prod_{i=1}^j \prod_{p=1}^k N_p^{(i)}!} \end{aligned} \quad (A1.2)$$

The total number of configuration becomes

$$\begin{aligned} W &= W_1 W_2 \\ &= \frac{N!}{\prod_{i=1}^j N^{(i)}!} \frac{\prod_{i=1}^j N^{(i)}!}{\prod_{i=1}^j \prod_{p=1}^k N_p^{(i)}!} \\ &= \frac{N!}{\prod_{i=1}^j \prod_{p=1}^k N_p^{(i)}!} \end{aligned} \quad (A1.3)$$

Making use of Stirling's approximation we may write

$$\ln W = N \ln N - \sum_{i=1}^j \sum_{p=1}^k N_p^{(i)} \ln N_p^{(i)} \quad (A1.4)$$

The statistical mechanical formulation of entropy  $S$  is given by

$$\begin{aligned} S &= k \ln W \\ &= k [N \ln N - \sum_{i=1}^j \sum_{p=1}^k N_p^{(i)} \ln N_p^{(i)}] \end{aligned} \quad (A1.5)$$

The system is isolated and is considered to be at thermodynamic equilibrium. Thus the entropy is a maximum, and

$$\begin{aligned}
 dS = 0 &= k \sum_{i=1}^j \sum_{p=1}^k \frac{\partial}{\partial N_p^{(i)}} \left[ N \ln N - \sum_{m=1}^j \sum_{n=1}^k N_n^{(m)} \ln N_n^{(m)} \right] dN_p^{(i)} \\
 &= -k \sum_{i=1}^j \sum_{p=1}^k \frac{\partial}{\partial N_p^{(i)}} \left[ N_p^{(i)} \ln N_p^{(i)} \right] dN_p^{(i)} \\
 &= -k \sum_{i=1}^j \sum_{p=1}^k [\ln N_p^{(i)} + 1] dN_p^{(i)} \quad (A1.6)
 \end{aligned}$$

or

$$\sum_{i=1}^j \sum_{p=1}^k [\ln N_p^{(i)} + 1] dN_p^{(i)} = 0 \quad (A1.7)$$

The system is subject to the restraints of constant number of molecules, constant total free volume and constant energy, so that

$$\sum_{i=1}^j \sum_{p=1}^k N_p^{(i)} = N \quad (A1.8)$$

$$\sum_{i=1}^j \sum_{p=1}^k e_i N_p^{(i)} = E \quad (A1.9)$$

$$\sum_{i=1}^j \sum_{p=1}^k v_p N_p^{(i)} = V_f \quad (A1.10)$$

or

$$\sum_{i=1}^j \sum_{p=1}^k dN_p^{(i)} = 0 \quad (A1.11)$$

$$\sum_{i=1}^j \sum_{p=1}^k e_i dN_p^{(i)} = 0 \quad (A1.12)$$

$$\sum_{i=1}^j \sum_{p=1}^k v_p dN_p^{(i)} = 0 \quad (A1.13)$$

Using the Lagrange undetermined multiplier procedure we may multiply equations (A1.11), (A1.12) and (A1.13) by  $(\alpha - 1)$ ,  $\beta$  and  $\Lambda$  respectively, and add the resulting equations to equation (A1.7), to give

$$\sum_{i=1}^j \sum_{p=1}^k [\alpha + \ln N_p^{(i)} + \beta e_i + \Lambda v_p] dN_p^{(i)} = 0 \quad (\text{A1.14})$$

Choosing suitable values for  $\alpha$ ,  $\beta$  and  $\Lambda$ , one may write

$$\alpha + \ln N_p^{(i)} + \beta e_i + \Lambda v_p = 0 \quad (\text{A1.15})$$

or

$$N_p^{(i)} = e^{-(\alpha + \beta e_i + \Lambda v_p)} \quad \text{for all } p, i \quad (\text{A1.16})$$

The probability distribution of free volume and energy may be written as

$$\begin{aligned} p_p^{(i)} &= \frac{N_p^{(i)}}{N} \\ &= \frac{e^{-(\alpha + \beta e_i + \Lambda v_p)}}{\sum_{i=1}^j \sum_{p=1}^k e^{-(\alpha + \beta e_i + \Lambda v_p)}} \end{aligned} \quad (\text{A1.17})$$

From equation (A1.16), on summing over  $p$  and  $i$ , we have

$$N = \sum_{i=1}^j \sum_{p=1}^k e^{-(\alpha + \beta e_i + \Lambda v_p)} \quad (\text{A1.18})$$

Solving for  $\alpha$  gives

$$e^{-\alpha} = \frac{N}{\sum_{i=1}^j \sum_{p=1}^k e^{-(\beta e_i + \Lambda v_p)}} \quad (\text{A1.19})$$

Making use of equations (A1.10), (A1.16) and (A1.19), and allowing the values of free volume  $v_k$  to tend to the continuum limit, we have

$$\begin{aligned}
 V_f &= \frac{\prod_{i=1}^j \prod_{p=1}^k e^{-(\beta e_i + \Lambda v_p)}}{v_p N e} \\
 &= \frac{\prod_{i=1}^j \prod_{p=1}^k e^{-\beta e_i} e^{-\Lambda v_p}}{N \prod_{i=1}^j e^{-\beta e_i} \prod_{p=1}^k v_p e^{-\Lambda v_p}} \\
 &= \frac{\prod_{i=1}^j e^{-\beta e_i} \prod_{p=1}^k e^{-\Lambda v_p}}{\prod_{i=1}^j e^{-\beta e_i} \prod_{p=1}^k v_p e^{-\Lambda v_p}}
 \end{aligned} \tag{A1.20}$$

thus

$$V_f = \frac{V_f}{N} = \frac{\int_0^\infty \tilde{v} e^{-\Lambda \tilde{v}} d\tilde{v}}{\int_0^\infty e^{-\Lambda \tilde{v}} d\tilde{v}} \tag{A1.21}$$

where  $\tilde{v}$  = fluctuating free volume

$$\text{or} \quad \Lambda = \frac{1}{v_f} \tag{A1.22}$$

Similarly combining equations (A1.9), (A1.16) and (A1.19) gives

$$\langle e \rangle = \frac{E}{N} = \frac{\sum_{i=1}^j e_i e^{-\beta e_i}}{\sum_{i=1}^j e^{-\beta e_i}} \tag{A1.23}$$

It is obvious from equation (A1.23) that  $\beta$  has its usual significance, that is

$$\beta = \frac{1}{kT} \tag{A1.24}$$

Equation (A1.17) can now be written as

$$\begin{aligned}
 p_p^{(i)} &= p(v_p) p(e_i) \\
 &= \frac{\exp(-v_p/v_f) \exp(-e_i/kT)}{\prod_{i=1}^j \prod_{p=1}^k \exp(-v_p/v_f) \exp(-e_i/kT)}
 \end{aligned} \tag{A1.25}$$

Since the values of  $v_p$  are assumed to be continuous, the summation can be replaced by an integral and the subscript  $p$  dropped, so that

$$p(\tilde{v}) = \frac{1}{v_f} \exp \left( - \frac{\tilde{v}}{v_f} \right) \quad (\text{A1.26})$$

To get an explicit expression for the energy distribution, Chung assumed the molecules to be harmonic oscillators. In the classical limit (172)

$$p(e) = \left( \frac{1}{2kT} \right) \left( \frac{e}{kT} \right)^2 \exp \left( - \frac{e}{kT} \right) \quad (\text{A1.27})$$

The probability that a molecule simultaneously has an energy greater than some value  $e_v$  and a free volume greater than some value  $v_o$  is:

$$\begin{aligned} p(\tilde{v} > v_o, e > e_v) &= \int_{v_o}^{\infty} \int_{e_v}^{\infty} p(\tilde{v}) p(e) de d\tilde{v} \\ &= \left[ \frac{1}{2} \left( \frac{e_v}{kT} \right)^2 + \left( \frac{e_v}{kT} \right) + 1 \right] \exp \left[ - \left( \frac{e_v}{kT} + \frac{v_o}{v_f} \right) \right] \end{aligned} \quad (\text{A1.28})$$

Based on the assumption that self-diffusivity and fluidity are directly proportional to this probability, one may write for the expressions of viscosity and self-diffusivity

$$\eta = A \exp \left[ \frac{E_v}{RT} + \frac{V_o}{V - V_o} \right] \quad (\text{A1.29})$$

and

$$D = B \exp \left[ - \left( \frac{E_v}{RT} + \frac{V_o}{V - V_o} \right) \right] \quad (\text{A1.30})$$

where

$$v_f = v - v_o$$

$$V = Nv$$

$$V_o = Nv_o$$

$$E_v = Ne_v$$

and A and B are assumed roughly constant. The form of the pre-exponential factors is not made clear in the derivation. The pre-exponential term appearing in equation (A1.28) depends on the assumed form of the molecular energy. Thus if the molecules are assumed to be in a potential well, rather than behaving as oscillators, a different pre-exponential factor is obtained.

APPENDIX 2

FURTHER TEST OF PROPOSED FREE VOLUME THEORY

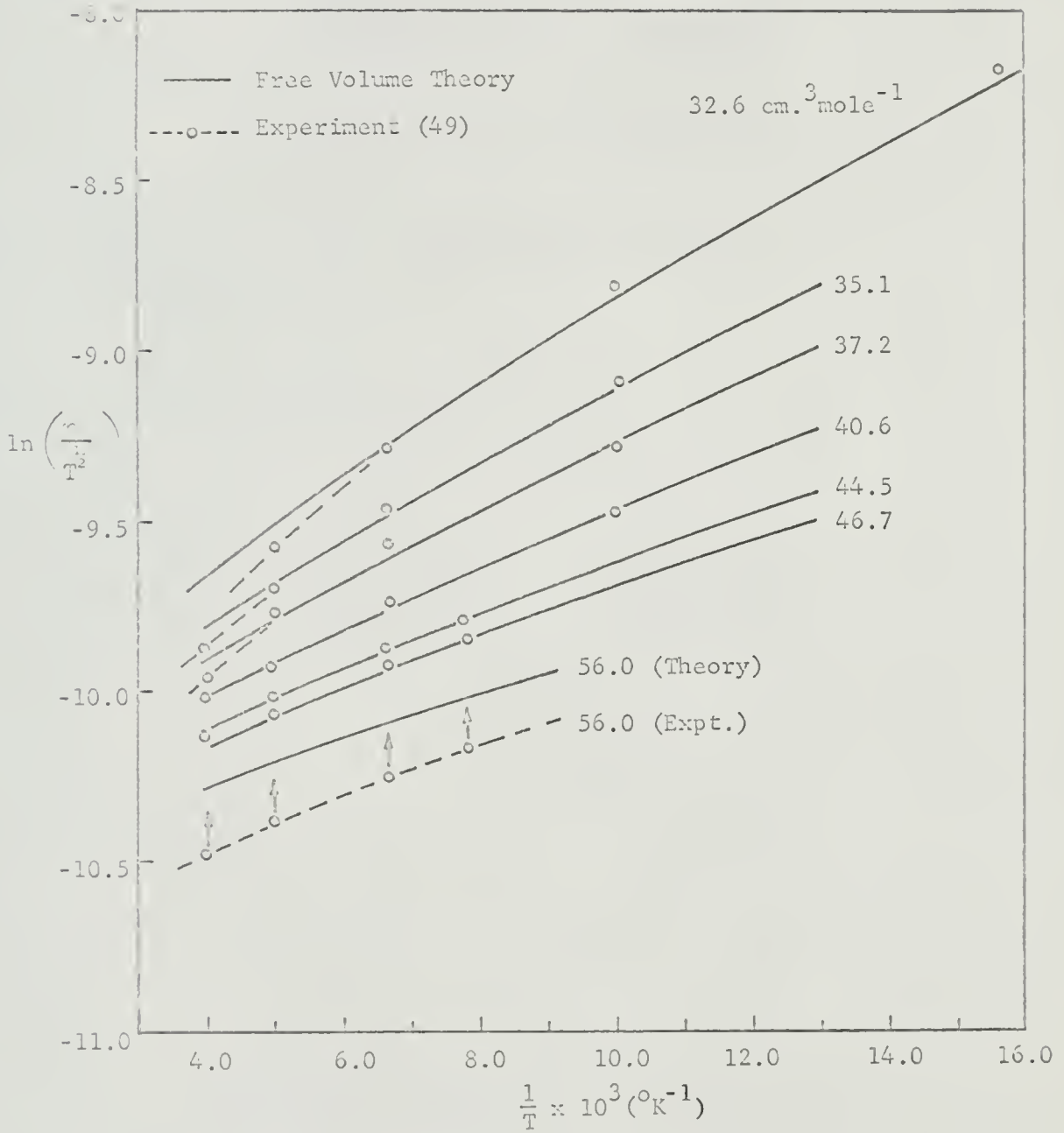


Figure A2.1. Test of Free Volume Theory for Liquid Nitrogen Viscosity.



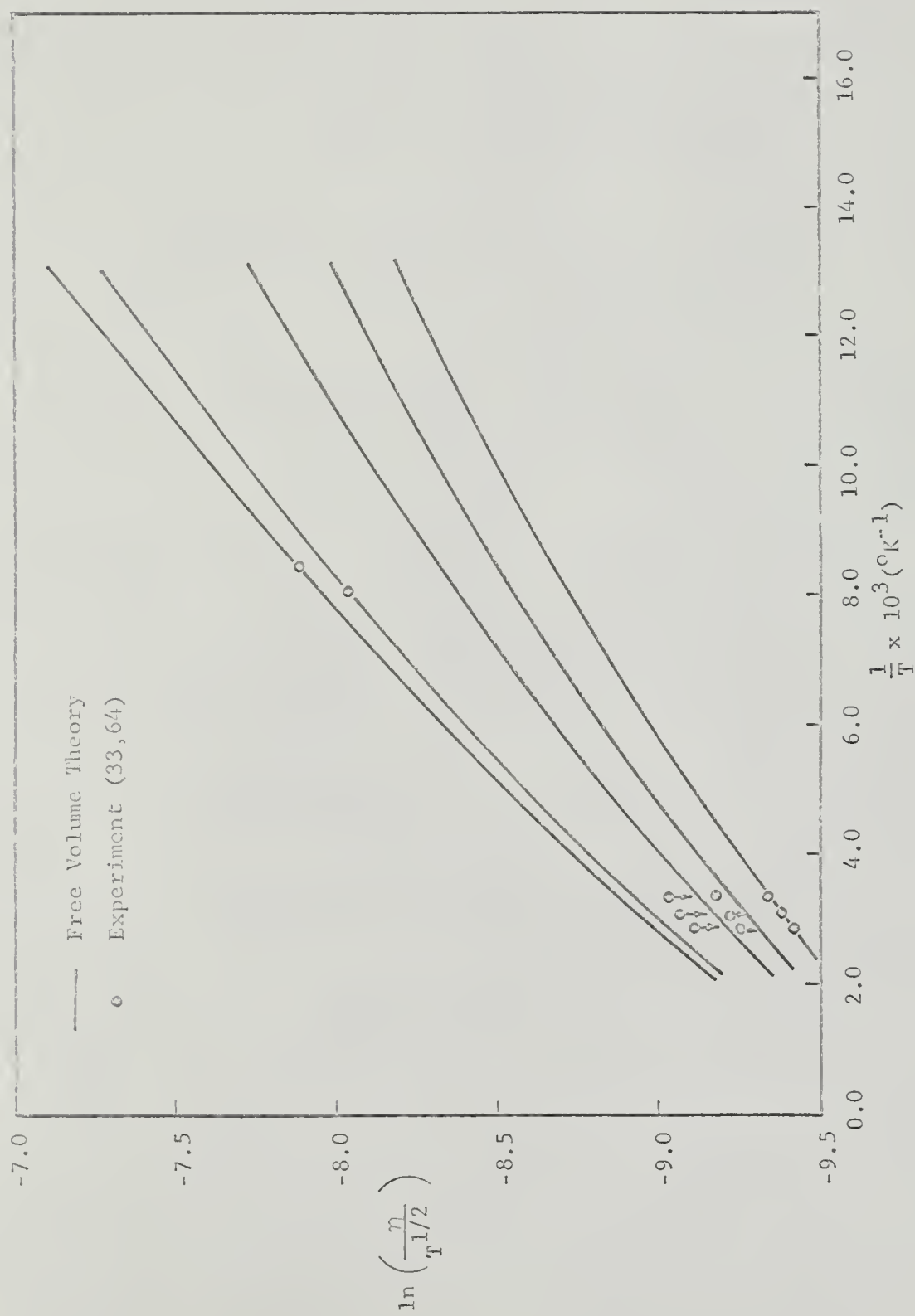


Figure A2.2. Test of Free Volume Theory for Liquid Krypton Viscosity.

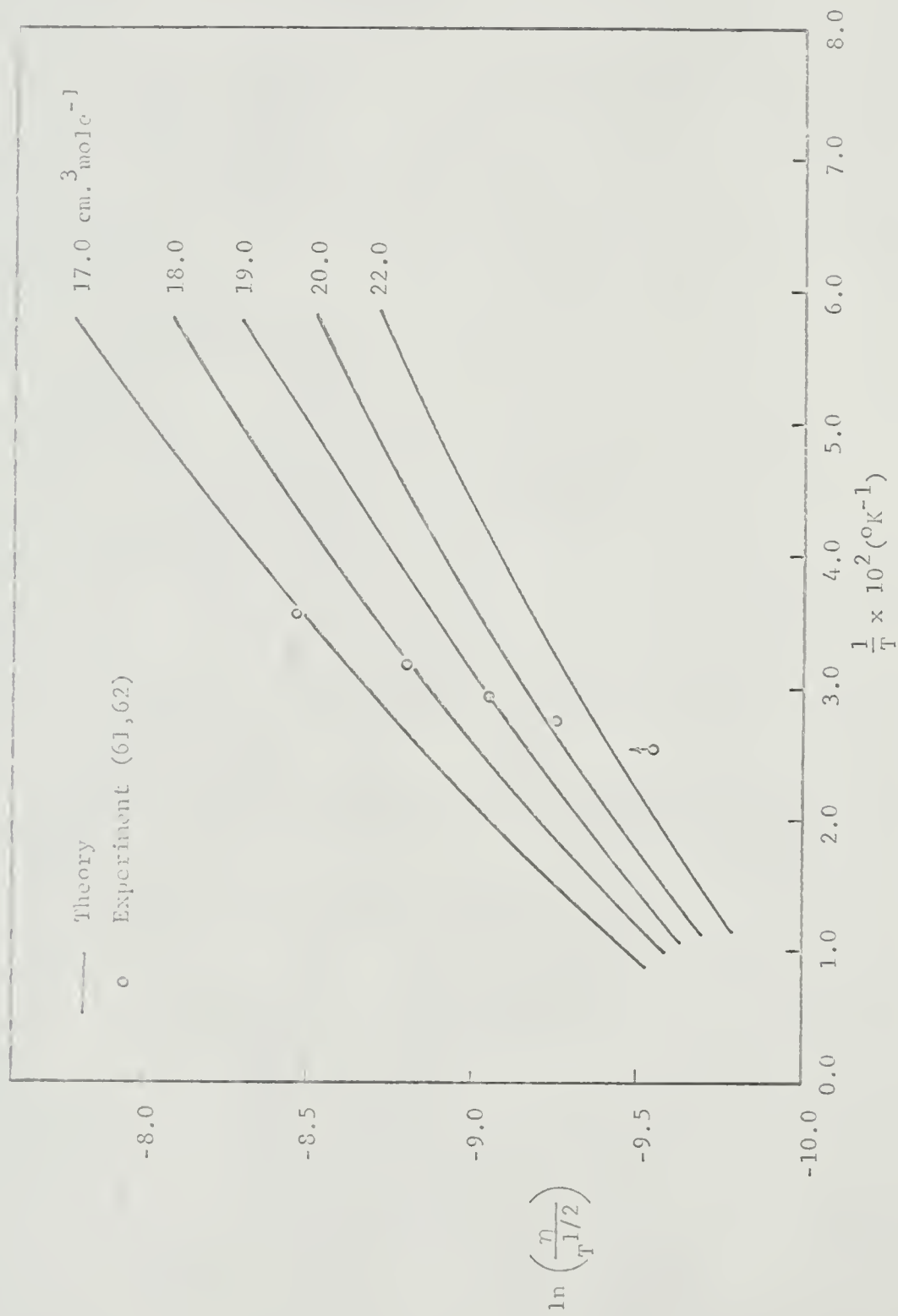


Figure A2.3. Test of Free Volume Theory for Liquid Neon Viscosity.

### APPENDIX 3

#### SOLUTION OF EQUATIONS OF MOTION FOR OSCILLATOR

From equations (6.15) and (6.17) we have

$$m \frac{d^2 x}{dt^2} + k_{11}x + k_{12}\Psi_x = 0 \quad (A3.1)$$

and

$$I \frac{d^2 \Psi_x}{dt^2} + k_{22}\Psi_x + k_{12}x = 0 \quad (A3.2)$$

In terms of differential operators one may write

$$(mD^2 + k_{11})x + k_{12}\Psi_x = 0 \quad (A3.3)$$

and

$$(ID^2 + k_{22})\Psi_x + k_{12}x = 0 \quad (A3.4)$$

Eliminating  $\Psi_x$  from equations (A3.3) and (A3.4) gives

$$(ID^2 + k_{22})(mD^2 + k_{11})x - k_{12}^2 x = 0 \quad (A3.5)$$

Expanding equation (A3.5) we have

$$[ImD^4 + (k_{22}m + k_{11}I)D^2 + k_{11}k_{22} - k_{12}^2]x = 0 \quad (A3.6)$$

Equation (A3.6) may be solved to give roots of D as

$$D = \pm i \left[ \frac{(k_{22}m + k_{11}I) \pm \sqrt{(k_{22}m + k_{11}I)^2 - 4Im(k_{11}k_{22} - k_{12}^2)}}{2Im} \right]^{1/2} \quad (A3.7)$$

Let

$$\omega_1 = \left[ \frac{(k_{22}^m + k_{11}I) - \sqrt{(k_{22}^m + k_{11}I)^2 - 4\text{Im}(k_{11}k_{22} - k_{12}^2)}}{2\text{Im}} \right]^{1/2} \quad (\text{A3.8})$$

$$\omega_2 = \left[ \frac{(k_{22}^m + k_{11}I) + \sqrt{(k_{22}^m + k_{11}I)^2 - 4\text{Im}(k_{11}k_{22} - k_{12}^2)}}{2\text{Im}} \right]^{1/2} \quad (\text{A3.9})$$

Therefore

$$x = A_1 e^{-i\omega_1 t} + A_2 e^{+i\omega_1 t} + A_3 e^{-i\omega_2 t} + A_4 e^{i\omega_2 t} \quad (\text{A3.10})$$

Similarly, eliminating  $x$  from equations (A3.3) and (A3.4) gives

$$(mD^2 + k_{11})(ID^2 + k_{22})\Psi_x - k_{12}^2 \Psi_x = 0 \quad (\text{A3.11})$$

Equation (A3.11) is expanded to give

$$[ImD^4 + (k_{22}^m + k_{11}I)D^2 + k_{11}k_{22} - k_{12}^2]\Psi_x = 0 \quad (\text{A3.12})$$

Solving for the roots of  $D$  we have

$$D = \pm i \left[ \frac{(k_{22}^m + k_{11}I) \pm \sqrt{(k_{22}^m + k_{11}I)^2 - 4\text{Im}(k_{11}k_{22} - k_{12}^2)}}{2\text{Im}} \right]^{1/2} \quad (\text{A3.13})$$

Making use of equations (A3.13), (A3.8) and (A3.9),

$$\Psi_x = E_1 e^{-i\omega_1 t} + B_2 e^{i\omega_1 t} + B_3 e^{-i\omega_2 t} + B_4 e^{i\omega_2 t} \quad (\text{A3.14})$$

Since we have assumed that the translational and angular oscillations represented by equations (A3.1) and (A3.2) are harmonic and that the oscillations are in phase, then  $\omega_1$ , which represents the angular

velocity of a harmonic motion, must be equal to  $\omega_2$ . This is true if

$$\sqrt{(k_{22}m+k_{11}I)^2 - 4\text{Im}(k_{11}k_{22}-k_{12}^2)} = 0 \quad (\text{A3.15})$$

Equation (A3.10) now reduces to

$$x = A'_1 e^{-i\omega_1 t} + A'_2 e^{i\omega_1 t} \quad (\text{A3.16})$$

$$\text{Since } e^{-i\omega_1 t} = \cos\omega_1 t - i\sin\omega_1 t \quad (\text{A3.17})$$

$$\text{and } e^{i\omega_1 t} = \cos\omega_1 t + i\sin\omega_1 t \quad (\text{A3.18})$$

Equation (A3.16) may be written as

$$x = A'\cos\omega_1 t + A''\sin\omega_1 t \quad (\text{A3.19})$$

where

$$A' = A'_1 + A'_2$$

$$A'' = i(A'_2 - A'_1)$$

Similarly equation (A3.14) may be written as

$$\Psi_x = B'\cos\omega_1 t + B''\sin\omega_1 t \quad (\text{A3.20})$$

# APPENDIX 4

## HAMILTONIAN FOR THE THREE-DIMENSIONAL OSCILLATOR

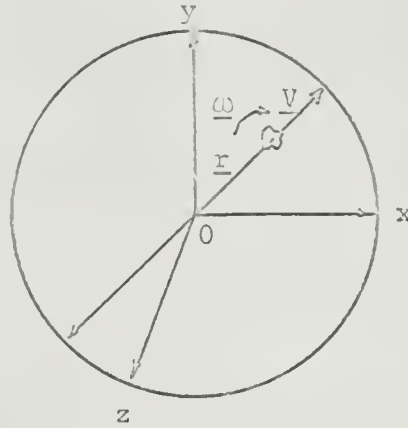


Figure A4.1. A Three-Dimensional Oscillator Model

Consider a molecule oscillating in an isotropic harmonic manner in a 3-dimensional cell. At any particular position  $\underline{r}$  of the molecule, it has a linear velocity  $\underline{V}(\underline{r})$  and an angular velocity  $\underline{\omega}(\underline{r}, \underline{\theta})$ , where  $\underline{\theta}$  represents the Eulerian angles.

One may resolve  $\underline{r}$  and  $\underline{V}(\underline{r})$  along the x, y and z axes as

$$\underline{r} = x\underline{e}_1 + y\underline{e}_2 + z\underline{e}_3 \quad (\text{A4.1})$$

$$\underline{V}(\underline{r}) = V_x(x)\underline{e}_1 + V_y(y)\underline{e}_2 + V_z(z)\underline{e}_3 \quad (\text{A4.2})$$

Let  $\underline{\omega}(\underline{r}, \underline{\theta})$  be made up of two parts; a constant angular velocity  $\underline{\omega}^0(\underline{r} = 0, \underline{\theta})$  together with a harmonic angular oscillator which is center of mass coordinates dependent,  $\underline{\omega}(\underline{r})$ , superimposed on it. In other words we assume

$$\underline{\omega}(\underline{r}, \underline{\theta}) = \underline{\omega}(\underline{r}) + \underline{\omega}^0(\underline{r} = 0, \underline{\theta}) \quad (\text{A4.3})$$

Resolving this along the 3 Cartesian coordinates we have

$$\begin{aligned}\underline{\omega}(\underline{r}, \underline{\theta}) = & \omega_x(x) \underline{e}_1 + \omega_y(y) \underline{e}_2 + \omega_z(z) \underline{e}_3 + \omega_x^o(\underline{\theta}) \underline{e}_1 \\ & + \omega_y^o(\underline{\theta}) \underline{e}_2 + \omega_z^o(\underline{\theta}) \underline{e}_3\end{aligned}\quad (\text{A4.4})$$

The angular velocities at the cell center can be expressed in terms of Eulerian angles as (173)

$$\omega_x^o(\underline{\theta}) = \dot{\theta} \cos \phi + \dot{\psi} \sin \theta \sin \phi \quad (\text{A4.5})$$

$$\omega_y^o(\underline{\theta}) = \dot{\theta} \sin \phi - \dot{\psi} \sin \theta \sin \phi \quad (\text{A4.6})$$

$$\omega_z^o(\underline{\theta}) = \dot{\phi} + \dot{\psi} \cos \theta \quad (\text{A4.7})$$

Suppose that the molecule is oscillating in a particular direction with instantaneous velocity  $\underline{V}$  at any position  $\underline{r}$ , and at the same time it has a harmonic angular oscillation which is in phase with the linear one.

We now consider the components of  $\underline{V}$  and  $\underline{\omega}(\underline{r}, \underline{\theta})$ . We pair  $(V_x, \omega_z)$ ,  $(V_y, \omega_x)$  and  $(V_z, \omega_y)$ , and consider them as the linear and angular velocities of 3 oscillators, one along the x-axis, one along the y-axis and one along the z-axis.

These oscillators may be considered separately. The oscillation associated with the x-axis will be as shown in Figure 6.3. We define the angles associated with  $\omega_x$  as

$$\theta_x(t) = \int_{t_0}^t \omega_x(x, \underline{\theta}) dt \quad (\text{A4.8})$$

$$\Phi_x(t) = \int_{t_0}^t \omega_x(\underline{\theta}) dt \quad (A4.9)$$

$$\Psi_x(x) = \int_{t_0}^t \omega_x(x) dt \quad (A4.10)$$

The potential and kinetic energies are expressed as before as

$$U_x(x, \Psi_x) = \frac{1}{2} k_{11} x^2 + k_{12} x \Psi_x + \frac{1}{2} k_{22} \Psi_x^2 \quad (A4.11)$$

$$K_x = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} I \dot{\Psi}_x^2 \quad (A4.12)$$

The equations of motion and their solution are now identical to those given in section 6.2. The final equations for the potential and kinetic energies associated with the x-direction are

$$\begin{aligned} U_x(x, \Psi_x) &= \frac{1}{2} c [k_{11} x^2 + k_{12} x \Psi_x] \\ &= \frac{1}{2} c [k_{11} + \Xi k_{12}] x^2 \end{aligned} \quad (A4.13)$$

$$K_x = \frac{1}{2} c m \dot{x}^2 \quad (A4.14)$$

where  $\Xi$  and  $c$  are defined by equations (6.32) and (6.37). Similarly for the y and z axes we have

$$U_y(y, \Psi_y) = \frac{1}{2} c [k_{11} + \Xi k_{12}] y^2 \quad (A4.15)$$

$$U_z(z, \Psi_z) = \frac{1}{2} c [k_{11} + \Xi k_{12}] z^2 \quad (A4.16)$$

$$K_y = \frac{1}{2} c m \dot{y}^2 \quad (A4.17)$$



$$K_z = \frac{1}{2} c m \dot{z}^2 \quad (\text{A4.18})$$

The Hamiltonian for the center of mass coordinates becomes

$$\begin{aligned} H_{CM} &= \sum_{i=1}^N \left[ K_{ix} + K_{iy} + K_{iz} + U_{ix} + U_{iy} + U_{iz} \right] + U(0,0) \\ &= \sum_{i=1}^N \left[ \frac{c}{2m} (p_{ix}^2 + p_{iy}^2 + p_{iz}^2) + \frac{1}{2} c(k_{11} + k_{12})(x_i^2 + y_i^2 + z_i^2) \right] + U(0,0) \\ &= \sum_{i=1}^N \frac{c}{2m} (p_{ix}^2 + p_{iy}^2 + p_{iz}^2) + cU(\underline{r}_1 \dots \underline{r}_N) \end{aligned} \quad (\text{A4.19})$$

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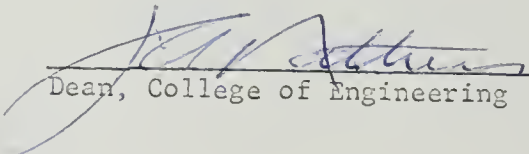
## BIOGRAPHICAL SKETCH

Mr. Min Jack Tham was born on April 14, 1935 in Shanghai, China. He received all his early education in Rangoon, Burma. In May, 1953, he entered the University of Rangoon and passed the Intermediate Science Examinations in March, 1955. He was admitted to the College of Engineering, University of Rangoon in the same year, and received a Bachelor of Science degree in Chemical Engineering in March, 1959. During his six years in the University of Rangoon, he passed each year's examinations (except the 3rd Year Engineering Examinations) with Distinction. From 1959 to 1963 he served at the Ngwe Zin Yan Oil and Flour Mills, Rangoon, as chief engineer.

In September, 1963, he came to the United States of America for graduate study in chemical engineering. He entered the University of Florida and received a M.S.E. degree in Chemical Engineering in December, 1964.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

June, 1968

  
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